REGISTERED NO. M. 3121

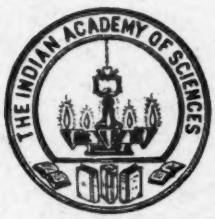
PROCEEDINGS

OF THE

INDIAN ACADEMY OF SCIENCES

VOL. V] *SECTION A* [NO. 4

APRIL, 1937



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PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, HEBBAL, BANGALORE.

DISPERSION OF DEPOLARISATION OF LIGHT-SCATTERING IN COLLOIDS.

Part II. Silver Sols.

By R. S. Krishnan.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received March 6, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

In Part I (Krishnan, 1937) of this series, it has been pointed out by the author that in order to determine the size and shape of colloidal particles it is important to make comparative studies of the dispersion of depolarisation of the transversely scattered light with the incident light in three different states of polarisation, namely, unpolarised, vertically polarised and horizontally polarised. A study of the dispersion of depolarisation of light-scattering in colloids is also important as it is connected with other well-known phenomena exhibited by colloidal solutions, namely, magnetic, electric and flow birefringence and their dispersion with wave-length. Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h with gold sols indicated that in the region of characteristic absorption, the depolarisation factors and consequently the anisotropy of the particles assume rather high values. From a comparison of the observed depolarisation and absorption curves with the theoretical ones, it has been concluded that the particles in gold sols behave optically like prolate ellipsoids with axial ratio equal to 0·7. In view of the interesting results obtained with gold sols, it was thought desirable to extend these optical investigations to a series of other sols.

In this paper the results obtained with a series of six unprotected silver sols prepared according to different methods are given. The approximate form of the silver particles in the colloidal state has also been determined.

2. Earlier Investigation.

The property of exhibiting a wide variety of colours is probably the most outstanding characteristic of colloidal silver. This was pointed out for the first time by Siedentopf (1910). On the basis of Mie's theory of the colour of metallic turbid media, Muller (1911) and Feick (1925) calculated the absorption coefficient of silver sols containing particles assumed to be

spheres of a given diameter. Feick had further deduced the alteration in colour that would occur with increase in the size of the particles. But it has been found by different observers that the colours of colloidal silver do not agree with these theoretical calculations. Gans (1915) has shown from theoretical considerations that the form of the particles in silver sols (as in gold sols) had a strong influence on the colour exhibited by them. From the observed absorption coefficients of collargol, he concluded that the silver particles were not spherical but were ellipsoidal in shape.

In a theoretical paper Gans (1921) has developed formulæ for the dispersion of refractive index and depolarisation of the light scattered by small colloidal silver particles of ellipsoidal shape. According to his theory the dispersion of refractive index of a sol containing spherical particles is normal while that of a sol containing ellipsoidal particles is anomalous. Some preliminary measurements of the depolarisation factor ρ_u of a silver sol were made by Gans (1921) and Isnardi (1921) for λ 5000 A.U., from which they concluded that the colloidal silver particles are prolate ellipsoids with the axial ratio slightly less than unity. But up till now, no detailed quantitative measurements have been made either of the dispersion of refractive index or the dispersion of depolarisation of light-scattering in silver sols.

3. *Preparation of the Sols.*

Six typical unprotected silver sols have been selected for the present investigation. Protected silver sols have been excluded because the results obtained with them will depend to a considerable extent on the nature of the protecting agent employed and consequently may not be easily amenable to theoretical interpretation.

Sol I was prepared by the well-known Bredig's method. An arc was struck between two pure silver electrodes immersed in double distilled conductivity water contained in a resistance glass beaker. The beaker was surrounded by ice. A current of about 5-6 amps. was passed just for a few seconds. The sol which resulted was allowed to stand for a day. After the heavy particles had settled down, the clear sol was decanted into a hard glass bottle which had previously been cleaned and well steamed. The sol is quite stable even after a month. The colour of the sol was greenish grey.

Sol II was a nuclear solution. This was prepared by adding 120 c.c. of double distilled water to 24 c.c. of a solution of pure silver oxide containing 0·001 per cent. silver. Two drops of an 0·18 N sodium carbonate solution were added to the silver solution followed by the addition of 1 c.c. of phosphorus solution prepared by diluting the saturated solution of phosphorus in ether twenty times with ether. The sol which resulted at once was slightly

yellowish in colour. This sol was used as the nuclear sol for the preparation of sols III, IV and V.

Sol III was prepared as follows. To 50 c.c. of silver oxide solution containing 0·0005 per cent. silver were added 1 c.c. of 0·18 N sodium carbonate, 10 c.c. of silver nuclear solution and 0·2 c.c. of hydrogen peroxide solution diluted to 1 part in 1000. The reaction took place rapidly, giving a clear sol containing bluish particles.

Sol IV was prepared according to the method suggested by Voigt. To 50 c.c. of a solution of silver oxide containing 0·0005 per cent. silver were added 0·2 c.c. of 0·18 N sodium carbonate and 20 c.c. of silver nuclear solution. The mixture was heated to boiling and was then reduced by 0·5 c.c. of formaldehyde solution prepared by diluting 2 c.c. of commercial formalin with 100 c.c. of water. A bright yellow clear sol formed at once.

Sol V was prepared according to the method recommended by Voigt and Heumann (1928) for the preparation of uniform sol with particles of approximately the same size and colour. To 50 c.c. of a solution of pure silver oxide containing 0·0005 per cent. silver were added 0·4 c.c. of 0·18 N sodium carbonate solution, 20 c.c. of nuclear solution and 2 c.c. of 0·0055 per cent. solution of hydrazine sulphate. Reduction took place at once with the formation of a light yellow clear sol.

It is well known that in the case of silver sols, most uniform sols result if a small amount of gold nuclear solution is used instead of silver nuclear sol. Sol VI was prepared according to this method. To 50 c.c. of a solution of silver oxide containing 0·0005 per cent. silver were added 0·3 c.c. of 0·18 N sodium carbonate solution and 0·5 c.c. of gold nuclear solution followed by the addition of 0·5 c.c. of hydrogen peroxide diluted to 1 part in 1000. An yellowish-brown sol resulted at once.

The sols were preserved in resistance glass bottles thoroughly cleaned and well steamed. The sols were not allowed to be unnecessarily exposed to light. Even after a month, the sols were quite stable.

4. Depolarisation Measurements.

Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h for the ultra-violet region were made by the same method as was employed for the depolarisation measurements with gold sols. The experimental set up has already been described in Part I (Krishnan, 1937) of this series. From a series of photographs taken, the readings of the nicol in the path of the scattered light, corresponding to the equality of intensity of the two mutually perpendicular components of the scattered light for the following wavelengths,

namely, 2967, 3650, 4046 and 4358 A.U. were read off and the depolarisation values were calculated therefrom. A correction arising from the finite angle of convergence of the incident beam had to be applied to the observed values of the depolarisation. The correction for ρ_u was equal to 0·15 per cent. The correction for ρ_v was half of that for ρ_u.

The sols examined did not show any appreciable fluorescence. This was evidenced from the clear picture (without any background) obtained by photographing through the spectrograph the light scattered by these sols when they were illumined with the light from a mercury arc.

For the visible region the method adopted was slightly different from the one employed for gold sols. Since the scattering was more intense in silver sols than in gold sols, measurements of the depolarisation factors ρ_u, ρ_v and ρ_h were made visually using a monochromator. The experimental set up is shown in Fig. 1.

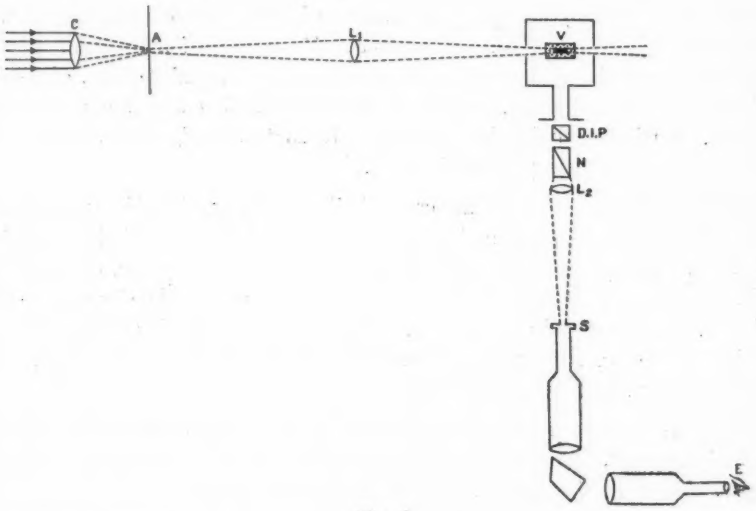

FIG. 1.

C = Condenser.
A = Square aperture (2 mm. square).
L_1 = Long focus photographic lens.
V = Cell containining the sol.
D.I.P. = Double-image prism.
N = Nicol (square ended).
L_2 = Lens.
S = Slit of a Hilger constant deviation spectroscope, which was used as a monochromator.
E = Eye of the observer.

A parallel beam of sunlight reflected by a single mirror (front silvered) Foucault Helistat was condensed by means of a long focus photographic lens C, on to the square aperture A. The axis of the collimator of the spectroscope was kept exactly normal to the incident beam. Before taking measurements the validity of the reciprocity theorem in silver colloids was tested out as follows. A double-image prism was placed in the path of the incident beam. The scattered light was viewed through another double prism. It was found that the middle two anisotropic components were exactly equal in intensity and colour, but they were more bluish than the outer two showing thereby that the depolarisation values would be greater for the blue region than for the yellow or red region. In sols IV and VI it was noticed that the fourth component was definitely brighter than the middle two.

The depolarisation factors were then measured as follows. The drum of the constant deviation spectroscope was set at readings corresponding to 4500, 5000, 5500, 6000 and 6500 A.U. Observing through the eye-piece, the nicol N was rotated and the rotation of the nicol was noted corresponding to the two adjacent positions of equality of intensity of the two components of the scattered light for each wave-length. The depolarisation factor was calculated from the mean value of the angle of rotation of the nicol. For polarising the incident beam a wide square-ended nicol was made use off. Thus ρ_u, ρ_v and ρ_h were determined experimentally for the sols I, III to VI for different wave-lengths.

As the intensity of scattering was very feeble in the nuclear sol, this method could not be applied. Using the point source mercury arc and the photographic method the values of ρ_u and ρ_v were determined for λ 2967, 3650, 4046, 4358, 5461 and 5790. The values of ρ_u and ρ_v corresponding to 4750, 5000 and 5500 were obtained by interpolation. The value of ρ_h was calculated from the observed values of ρ_u and ρ_v.

A correction arising from the finite angle of the incident beam was also applied to the observed values of ρ_u and ρ_v. The corrected values are given in Tables I and II.

TABLE I. *Dispersion of Depolarisation.*

Wavelength λ in A.U.	Silver Sol I (Bredig's sol)			Silver Sol II (Nuclear sol)			Silver Sol III (H_2O_2 reduction)		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	6·7	2·0	57	6·2	3·4	100	11·5	..	..
3650	12·5	4·9	93	7·2	4·2	100	14	4·9	49
4046	22·7	11	83	14	7·2	100	24·8	10	63
4358	30·7	17	100	12·5	6·2	100	27	11·2	68
4750	32	19·8	100	11	5·5	100	29·5	19·8	100
5000	33·3	20	100	10·5	5·2	100	29	19·8	100
5500	36	21·8	100	10	4·9	100	27·5	18	100
6000	38·3	23·8	100	..	..	..	26	16·3	100
6500	39	25·5	100	..	..	..	25·5	14	87

TABLE II. *Dispersion of Depolarisation.*

Wavelength λ in A.U.	Silver Sol IV (Formaldehyde reduction)			Silver Sol V (Hydrazine sulphate reduction)			Silver Sol VI (Au sol used as nuclear sol)		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	2·5	..	..	11·5	..	..	4·5	..	..
3650	6·2	2·2	63	18·9	7·2	78	8·8	3·1	61
4046	19	10·5	84	30·7	15·6	87	21·7	10·2	70
4358	22·8	12·5	95	34·7	17·2	100	27	13	75
4500	22·8	13·2	100	29·4	16·2	100	32	16·3	78
5000	16·3	6·4	100	24·8	14	100	42	21·4	81
5500	12·5	5·8	93	20·7	11·5	100	33·3	17·4	78
6000	10·2	4·9	87	18	10·5	100	30·7	17	90
6500	9·6	4·9	80	17	9·3	100	28·5	16·7	96·5

TABLE III.

Absorption Coefficient of Silver Sols.

Wave-length	Sol I	Sol II	Sol III	Sol IV	Sol V	Sol VI
2250	0·38	0·15	0·15	0·325	0·3	0·225
2500	0·23	0·12	0·135	0·24	0·21	0·22
2750	0·21	0·08	0·12	0·17	0·14	0·2
3000	0·275	0·05	0·1	0·11	0·07	0·15
3250	0·39	0·04	0·09	0·06	0·05	0·09
3500	0·55	0·13	0·12	0·19	0·22	0·19
3750	0·78	0·3	0·2	0·37	0·41	0·26
4000	0·98	0·52	0·28	0·6	0·6	0·32
4250	1·05	0·32	0·3	0·74	0·55	0·33
4500	1·05	0·18	0·275	0·6	0·4	0·3
5000	0·8	0·075	0·18	0·28	0·16	0·23
5500	0·625	0·05	0·12	0·15	0·08	0·14
6000	0·53	0·04	0·1	0·08	0·05	0·08
6500	0·45	0·02	0·08	0·045	0·03	0·07
7000	0·4	0·01	0·065	0·03	0·02	0·06

Sols I, III, IV and V were diluted three times and the measurement of ρ_u for two wave-lengths was repeated and it was found that no appreciable change in the value of ρ_u was produced by dilution showing thereby that the sols could be taken as optically infinitely dilute.

The values of ρ_u were plotted against wave-length. The curves are reproduced in Figs. 2 and 3.

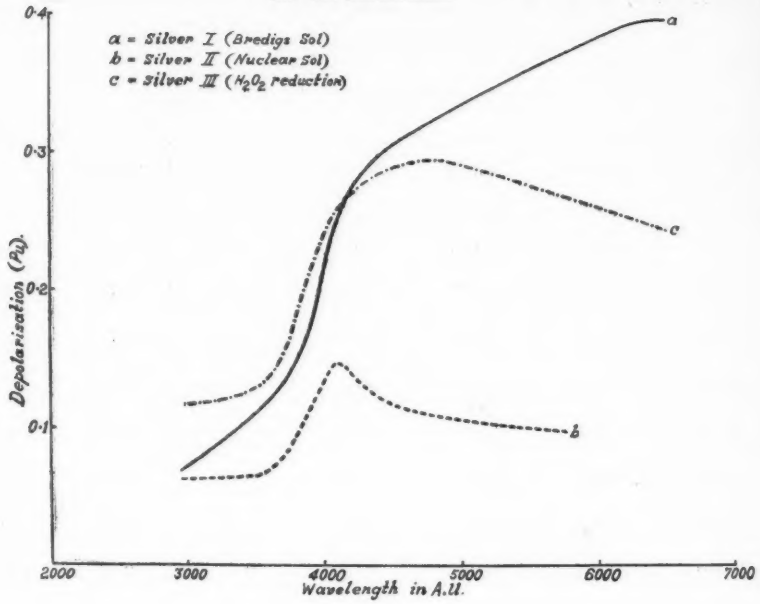
a = Silver I (Bredigs Sol)
b = Silver II (Nuclear Sol)
c = Silver III (H_2O_2 reduction)
Depolarisation (P_u).
0·4
0·3
0·2
0·1
2000
3000
4000
5000
6000
7000
Wavelength in A.U.
a
b
c

FIG. 2.

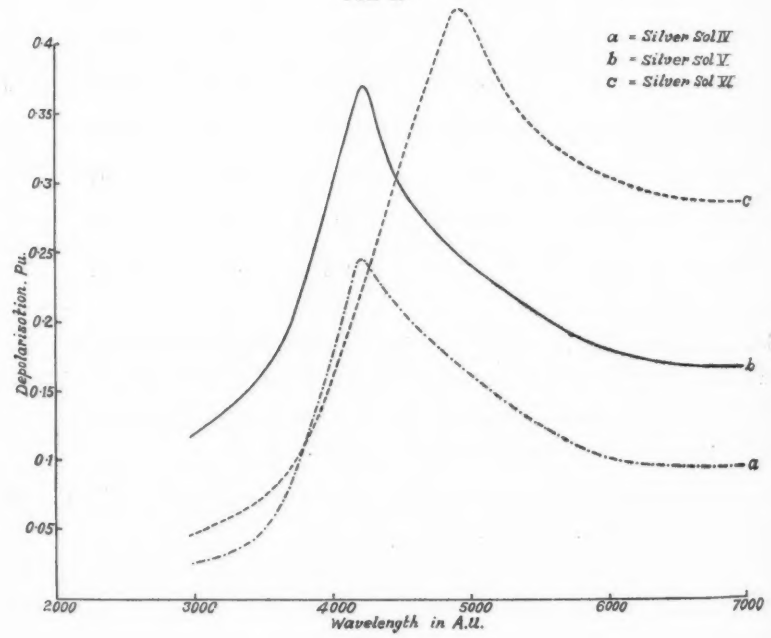
a = Silver Sol IV
b = Silver Sol V
c = Silver Sol VI
Depolarisation. Pu.
0·4
0·35
0·3
0·25
0·2
0·15
0·1
0·05
2000
3000
4000
5000
6000
7000
Wavelength in A.U.
a
b
c

FIG. 3.

5. *Absorption Measurements.*

The absorption measurements were made with a spekker ultra-violet photometer. The extinction coefficient per centimetre length of solution was determined for a series of wave-length from 2500 A.U. to 7000 A.U. The values are given in Tables III. The curves of absorption are plotted with extinction coefficient as ordinate and wave-length as abscissæ.

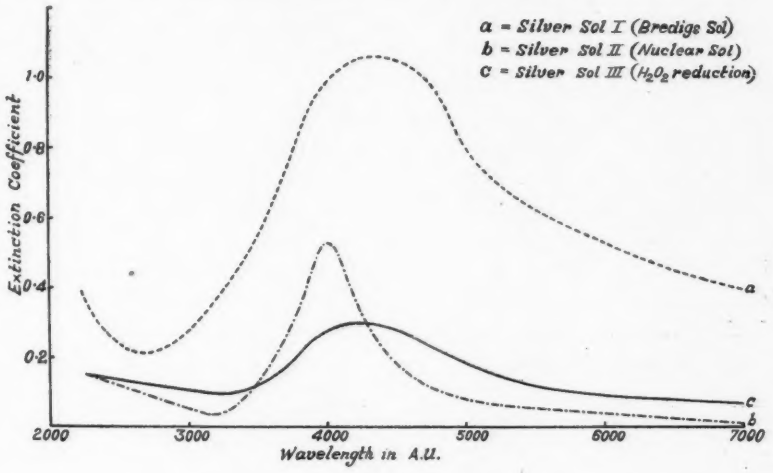

FIG. 4.

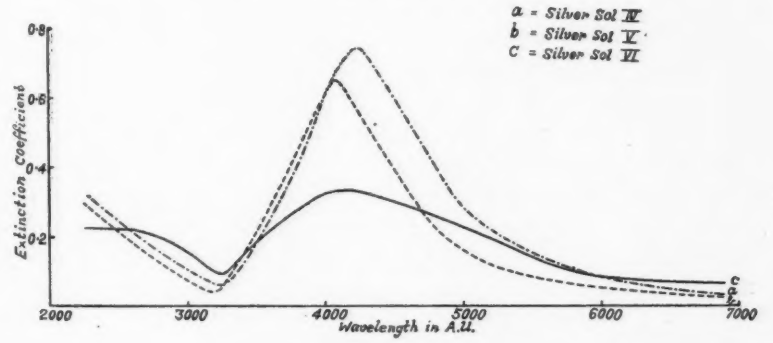

FIG. 5.

6. *Results.*

As in the case of gold sols, so also in silver sols ρ_u, ρ_v and ρ_h are markedly functions of wave-length. In all the sols studied except in Bredig's sol, *i.e.*, (sol I), starting from 3000 A.U. ρ_u goes on increasing, attains a maximum

in the region of maximum absorption and diminishes with further increase of wave-length. In sol I ρ_u goes on increasing continuously with increase of wave-length. The depolarisation curves for all the sols show a pronounced asymmetry about the point of maximum depolarisation, the curves being steeper on the shorter wave-length side than on the longer wave-length side. This is also the case with the absorption curves. ρ_v follows the same course as ρ_u. In the region of the characteristic absorption there is an increase of the optical anisotropy as is evinced by the notable increase of ρ_v. For the nuclear sol ρ_h has its limiting value of 100 per cent. from $\lambda = 3000$ to $\lambda = 6000$ A.U. In sols I, III and V ρ_h is less than 100 per cent. in the ultra-violet region, whereas, in sol IV ρ_h is less than 100 per cent. throughout except in the region of the characteristic absorption where it attains its limiting value of 100 per cent. In sol VI ρ_h is less than 100 per cent. throughout and it increases or decreases with wave-length *pari passu* with ρ_u. A comparative study of the values of ρ_h for all the sols indicates that the nuclear sol contains particles of extremely small size, while in sols IV and VI the size of the particles becomes comparable with the wave-length of light. Sols I, III and V contain particles of intermediate sizes.

As has been observed previously, the curves of absorption show a pronounced maximum in the violet region, *i.e.*, at about 4200 A.U. for all the sols. There is a distinct minimum in the ultra-violet region at about 3200 A.U. for all the sols except for the Bredig's sol for which the minimum is shifted further towards the shorter wave-length side. Although the depolarisation curves show a maximum in the violet region where the absorption is maximum it is not possible to detect a minimum at about 3200 A.U. in the depolarisation curves corresponding to the point of minimum absorption using mercury arc as the source of ultra-violet radiation since it does not give rise to any intense line in this region. The maximum and minimum of the absorption curve for sol III are much flatter than for any other sol. This is because the sols obtained by reduction with hydrogen peroxide using silver nuclear sols contain particles of varied sizes. The points of maximum and minimum absorption are different for different particle sizes. It has often been remarked that this method of preparation of the sol is quite unsatisfactory. The maximum of the absorption curve for sol VI is also rather flat, although it contains particles of uniform size. According to Mie's theory as the size of colloidal metal (silver or gold) particles increases, the maximum value of the absorption curve increases and it shifts to the longer wave-length side, up to a certain critical value for the size of the particles. Any further increase in size of the particles, lowers the maximum value and consequently the curve becomes flatter and flatter. This fact has been beautifully

illustrated in Figs. 4 and 5. From a comparison of the observed absorption curves for sols II, V, IV and VI and from what has been mentioned above it follows that $r_{II} < r_V < r_{IV} < r_{VI}$ where r_{II}, r_V, r_{IV} and r_{VI} are the diameters of the particles in sols II, V, IV and VI respectively. This is also in accordance with the depolarisation measurements of the author (see Tables I and II). In the Bredig's sol the absorption is relatively greater and the maximum extends over a wider range of wave-length than in any other sol. This is due to the presence of silver hydroxide in the sol and also due to the presence of particles of varied sizes.

7. *Theoretical Discussion.*

The values of the depolarisation factor ρ_u are evaluated from Gans' formula for very small particles of ellipsoidal shape. Table IV gives the comparative values of the depolarisation ρ_u for small elongated and flattened rotation ellipsoids.

TABLE IV.

Values of ρ_u (calculated).

B/A	Elongated rotation ellipsoid					Sphere	Flattened rotation ellipsoid		
λ in A.U.	0·00 %	0·23 %	0·57 %	0·77 %	1 %	1·60 %	2·63 %	10 %	∞ %
3500	22·9	18·4	8·1	2·8	0·0	32·9	64·9	70·2	52·4
4000	74·7	51·3	54·7	38·0	0·0	31·8	38	49·8	41·9
4200	69·7	73·5	70·2	27·7	0·0	18·6	29·9	38·7	40·7
4500	81·7	83·2	47·4	11·1	0·0	11·5	22·1	33·7	35·7
5500	83·8	75·1	24·7	5·1	0·0	7·4	16·5	26·5	30·9
6500	71·5	50·3	11·7	2·4	0·0	4·6	11·6	22·4	25·9
7500	62·8	44·4	9·9	2·1	0·0	4·1	10·5	21·1	24·7

According to Gans' theory for a flattened rotation ellipsoid the maximum of the depolarisation curve should lie in the ultra-violet region, *i.e.*, below 3500 A.U. whereas for an elongated ellipsoid or a prolate spheroid it is shifted towards the longer wave-length side of the region of characteristic absorption maximum. The latter corresponds to the experimentally observed data. Comparing the theoretical values of ρ_u with the experimental values it is seen that the particles in silver sols are more like elongated rotation ellipsoids

with the axial ratio equal to 0·75. The theoretical curves of the dispersion of ρ_u for elongated ellipsoidal particles having an axial ratio = 0·75 shows also an asymmetery about the point of maximum depolarisation. The observed values of ρ_u for regions of the spectrum far away from the region of characteristic absorption and on either side of it are higher than the calculated values of ρ_u for prolate ellipsoids having an axial ratio 0·75. This is because in these regions the anisotropy of the particles is smaller and hence the finite size of the particles enhances the observed depolarisation. Gans' theory is true only for particles of molecular dimensions. In the region of characteristic absorption the agreement is more perfect because the anisotropy is much greater and consequently the size effect is completely subdued.

The following table gives the absorption constant $k \times 10^{-3}$ for different wave-lengths calculated according to Gans, for very small particles of ellipsoidal shape. The values are taken from Gans' paper. The values of k given in the table below for an elongated rotation ellipsoid with the axial ratio B/A = 0·8 are obtained by interpolation.

TABLE V.

Absorption Coefficient (calculated).

B/A / λ in A.U.	Elongated rotation ellipsoid					Sphere	Flattened rotation ellipsoid			
	0·00	0·23	0·57	0·77	0·8	1·0	1·61	2·63	10	∞
3500	86·9	61·2	35·4	29·8	29	27·9	41·6	100·3	13·6	8·1
3750	75	127·6	258·2	194·9	189	152·3	101·1	30·5	9·7	6·6
4000	18·8	27·5	81·0	199·1	218	353·7	185·4	49·5	11·3	7·0
4200	11·2	16·5	77·2	202·9	188	93·5	343·4	114·9	13·5	7·5
4500	7·8	13·6	240·1	45·1	38	27·5	68·8	464·6	182·3	8·4
5000	6·7	19·1	34·8	11·5	11	9·1	15·3	63·4	34·2	10·4
5500	7·5	97·8	11·1	5·5	5·3	4·8	6·9	18·9	76·7	13·0
6000	8·4	24·9	5·6	3·2	3·2	2·8	3·9	9·0	224·9	16
6500	9·8	10·8	3·3	2·1	2·0	1·9	2·5	5·2	817·5	18·6
7000	10·4	6·1	2·2	1·5	1·4	1·3	1·7	3·4	405·1	20·1

A comparative study of the Tables III and V shows that the experimentally determined curves are similar to the theoretical curves calculated according to Gans' theory for elongated rotation ellipsoids of axial ratio equal to 0·8.

It is clear from the above considerations that the particles of silver in the colloidal state are not spherical in shape but behave optically as elongated ellipsoids with an axial ratio of 0·75 or 0·8.

It will be of interest to study the dispersion of refractive index of these silver sols and to correlate the results with the shape of the particles. This will be taken up as early as possible.

8. Other Experimental Evidence.

The double refraction in silver sols produced by mechanical flow has been investigated by Bjornstahl (1924). He observed negative streaming double refraction in some silver sols. The protected silver sol prepared according to Gutbier showed a positive effect. This is because the sol is really a silver oxide sol. Let us suppose that the particles can be represented as ellipsoids of revolution. The direction of flow is parallel to Z-axis in a co-ordinate system X, Y, Z, while the light is passed along the axis Y. If we consider the simple case of complete orientation, all the particles will be oriented in such a way that the greatest axis of the ellipsoid is parallel to the Z-axis, *i.e.*, to the direction of flow. The expression for the phase difference between the vibrations parallel to the Z-axis and to the X-axis respectively as derived by Bjornstahl (1924), is given by

$$\frac{n_z - n_x}{n_0} = \frac{N \pi v}{{n_0}^2} \left\{h' - h\right\}^{\text{Real}}$$

where N = number of particles per unit volume ;

n_0 = refractive index of the dispersion medium ;

$\frac{n}{n_0}$ = refractive index of colloid ;

v = volume of the ellipsoid ;

$$h = {n_0}^2 \frac{m'^2 - 1}{4\pi + (m'^2 - 1)\,P};$$

$$h' = {n_0}^2 \frac{m'^2 - 1}{4\pi + (m'^2 - 1)\,P'};$$

$$m' = \frac{m}{n_0};$$

m = complex refractive index for the disperse phase and

$$P = 4\pi \frac{1 - e^2}{e^2}\left[\frac{1}{2e} \log \frac{1 + e}{1 - e} - 1\right] \text{ for a prolate spheroid;}$$

$$P = \frac{4\pi}{e^2}\left(1 - \frac{\sqrt{1 - e^2}}{e} \text{ arc sin } e\right) \text{ for an oblate spheroid ;}$$

$$P + 2P' = 4\pi.$$

$\frac{3P}{4\pi}$ is less than unity for an elongated rotation ellipsoid, while it is greater than unity for a flattened rotation ellipsoid. $\frac{3P'}{4\pi}$ is greater than unity for an elongated one and less than unity for a flattened one.

In the case of silver for $\lambda = 6000$ A.U. $(h' - h)^{real}$ is negative for an elongated rotation ellipsoid. This gives rise to a negative flow birefringence $(h' - h)^{real}$ is positive for a flattened rotation ellipsoid. The negative effect at 6000 A.U. observed by Bjornstahl in silver sols indicates, therefore, that the particles are not spherical in shape but are elongated. The dispersion of flow birefringence in silver sols has not yet been studied. A large dependence of flow double refraction on wave-length should be expected from consideration of the dispersion of refractive index and anisotropy of colloidal silver particles.

Bergholm and Bjornstahl (1920) have shown that silver sols exhibit distinct negative double refraction in an electrical field. The electric double refraction is attributed to an orientation of silver particles of asymmetric shape. In the electric field the largest axis of the ellipsoid has a tendency to place itself parallel to the lines of force. Since the particles are charged cataphoresis takes place owing to the influence of the field. A body of asymmetric shape moving in a liquid tries to place its greatest axis at right angles to the direction of movement. These two opposing forces act on the particles. By comparison with the experiment on mechanical double refraction a negative electric double refraction indicates a resultant orientation along the direction of the field and an elongated ellipsoidal shape for the silver particles.

Silver sols should not, in general, exhibit any magnetic double refraction since silver, just like gold, is diamagnetically isotropic, and since X-ray analysis discloses that the particles in the colloidal state exhibit a crystal structure similar to that of silver in mass. This is in accordance with the observations of Bjornstahl (1924) and also with the recent observations of Nilakantan (1937). Only silver sols prepared according to Carey-Lea showed a strong negative effect. This is due to the contamination of the sol with iron to the extent of 0·3 to 1 per cent. of the silver quantity.

When silver sols are examined under a Cardioid ultra-microscope, scintillations are observed. Spherical particles scatter light symmetrically, while non-spherical ones scintillate because the scattered light is more intense when the particle, in the course of Brownian Movement lies with its long axis in the plane of the microscope and at right angles to the illuminating light.

It has been found by Levi and Tabet (1933) that when silver is deposited electrolytically growth takes place in a direction perpendicular to the octahedral faces. Since X-ray analysis discloses that the particles in silver sols

consist of crystals similar to those of silver in mass, the primary units are probably minute octahedra. The volume of an octahedron of side a, is equal to $\frac{\sqrt{2}}{3}a^3$, *i.e.*, $0{\cdot}47\ a^3$. The volume of the sphere circumscribed round the octahedron is equal to $\frac{\sqrt{2}}{3}\pi a^3$, *i.e.*, $1{\cdot}5\ a^3$. A prolate spheroid of axial ratio $0{\cdot}8$ can be inscribed inside the octahedron touching the four square edges. The semi-minor axis of such a spheroid would be equal to half the side of the octahedron, *i.e.*, $\frac{a}{2}$ and its volume is equal to $\frac{\pi}{4{\cdot}8}a^3 = 0{\cdot}65a^3$ which does not differ so greatly from that of the octahedron as the volume of the circumscribed sphere. It is thus permissible to consider the colloidal silver particles which are minute octahedra as optically equivalent to prolate spheroids of axial ratio $0{\cdot}8$ and not as spheres.

In conclusion, the author takes this opportunity to thank Prof. Sir C. V. Raman for his kind and helpful interest in the work.

9. *Summary.*

Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h and the extinction coefficient of a series of six silver sols are made for different wave-lengths from 2500 A.U. to 7000 A.U. As in the case of gold sols, so also in silver sols in the region of the characteristic absorption the depolarisation factors show an enormous increase. The optical anisotropy of the silver particles in the colloidal state is rather low in the ultra-violet and the red regions, whereas it assumes rather high values in the violet region where the absorption is maximum. Compared with the sols prepared according to other methods Bredig's sol behaves anomalously. Depolarisation measurements indicate that the nuclear sol contains particles of very small size, while the sols prepared by using formalin as reducing agent and that got by employing gold nuclear solution and hydrogen peroxide as reducing agent contain particles of size comparable with the wave-length of light. In the other sols the particles are of intermediate sizes. The observed values of the extinction coefficient and the depolarisation factor ρ_u are compared with the values calculated according to Gans' theory. From both these considerations it is inferred that the particles in silver sols behave optically like elongated ellipsoids with the axial ratio equal to $0{\cdot}75$. It is further suggested that the colloidal particles of silver may be in the form of minute octahedra which can be considered as optically equivalent to a prolate spheroid of the axial ratio stated above. The negative streaming double refraction and the negative electric double refraction observed by the earlier investigators are explained on the basis of the elongated ellipsoidal shape of the silver particles.

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DERIVATIVES OF SALICYLIC ACID.

Part XI. Bromo-Salicylic Acids and their Methyl Ethers.

By N. W. Hirwe and B. V. Patil.

(From the Royal Institute of Science, Bombay.)

Received March 19, 1937.

(Communicated by Dr. T. S. Wheeler, Ph.D., F.I.C., F.Inst.P., M.I.Chem.E.)

A detailed study of these acids was undertaken as their chloralamides were required for other work.

Salicylic acid has been brominated by various workers, with the result that together with 5-bromo-salicylic acid, there were obtained bromo-phenols and dibromo-salicylic acid. 3-Bromo-salicylic acid is not produced by direct bromination and has hitherto been produced only indirectly from 5-nitro-salicylic acid[1] in poor yield. A method has now been developed by which it can be obtained in a good yield, by passing superheated steam at 125°–135°, into a sufficiently concentrated aqueous solution of 3-bromo-5-sulpho-salicylic acid, the latter being prepared by bromination of 5-sulpho-salicylic acid; or by hydrolysis of bromo-chloral-salicylamide, formed by the bromination of chloral-salicylamide. Improved methods for 5-bromo and 3 : 5-dibromo-salicylic acids are also been described. Formation of a single substance or a mixture of several, depends on the rate of adding bromine to the reaction-mixture.

Peratoner[2] methylated these acids with methyl iodide; the use of dimethyl-sulphate has been described here. Excepting the 5-bromo acid, it is not possible to obtain them by the bromination of the methyl ethers of salicylic acids; with continued bromination and accumulation of the hydrobromic acid in the reaction, the $-OCH_3$ group is converted into the $-OH$ group and 3 : 5-dibromo-salicylic acid is obtained.

The ester of 3-bromo-salicylic acid is prepared from its silver salt, as the usual method of alcoholysis of either the acid or its chloride, failed; the amide, too, could only be obtained from the ester and not from the chloride. The other acids including the 3 : 5-dibromo acid, behave normally.

Experimental.

5-Bromo-salicylic acid.—Bromine (12 g.) was slowly aspirated through a solution of salicylic acid (10 g.) in acetic acid at 25°–30°. The reaction mixture

was allowed to stand overnight and then diluted. The solid obtained was recrystallised from acetic acid in needles, m.p. 163°–164° (Lit. 161° –165°).

Sodium salt.—Crystallises from water in short white needles. (Found: Na, 9·6; $C_7H_4O_3BrNa$ requires Na, 9·6 per cent.)

Potassium salt.—Crystallises from water: clusters of flakes. (Found: K, 15·3; $C_7H_4O_3BrK$ requires K, 15·3 per cent.)

Calcium salt.—Crystallises from water with four molecules of water: in gray-coloured short needles. (Found: Ca, 7·0; H_2O, 13·4; $C_{14}H_8O_6Br_2Ca$, $4H_2O$ requires Ca, 7·3; H_2O, 13·2 per cent.)

3 : 5-*Dibromo-salicylic acid.*—Bromine (58 g.) in acetic acid was gradually added during six hours, to a solution of salicylic acid (28 g.) in acetic acid, at 100°. On keeping it overnight crystals of dibromo acid separated. A further yield was obtained on dilution of the mother-liquor. It crystallises from acetic acid in rectangular crystals, m.p. 223°. (Lit. 218°; 223°.)

Sodium salt.—Crystallises from water in long shining needles with $1\frac{1}{2}$ mols. of water. (Found: Na, 6·4; H_2O, 7·7; $C_7H_3O_3Br_2Na$, $1\frac{1}{2}H_2O$ requires Na, 6·7; H_2O, 7·8 per cent.)

Potassium salt.—Crystallises from water in grains. (Found: K, 11·3; $C_7H_3O_3Br_2K$ requires K, 11·7 per cent.)

Calcium salt.—Crystallises from water in needles with six mols. of water. (Found: Ca, 5·4; H_2O, 14·8; $C_{14}H_6O_6Br_4Ca$, $6H_2O$ requires Ca, 5·4, H_2O, 14·6 per cent.)

3-*Bromo-salicylic acid.*—Method I: Salicylic acid (100 g.) is sulphonated by heating with concentrated sulphuric acid (200 c.c.) at 100° for half an hour. The sulphonic acid which separates is filtered, dissloved in a minimum quantity of water and bromine (105 g.) vapour is aspirated through it. The solution containing 3-bromo-5-sulpho-salicylic acid is concentrated until its boiling temperature reaches 125°. Superheated steam is then passed through it, the temperature being not allowed to rise above 135°, until no more of the bromo-acid separates. Further yield is obtained by filtering off the liberated acid and passing more steam into the filtrate. A higher temperature than 135° leads to the production of bromo-phenols. (Meldrum and Shah[3] pass steam into a solution to which phosphoric acid is added. They distil it at 155° with superheated steam, consequently much bromo-phenol is produced.) The product crystallised from alcohol in needles, m.p. 182°–183°. (Lit. 184°; 184°·5).

Method II: Bromine (8·7 g.) vapours were rapidly aspirated through an acetic acid solution of chloralsalicylamide when a solid separated. It crystallised from alcohol: short plates: m.p. 239°. This solid on hydrolysis with alkali yields 3-bromo-salicylic acid.

Sodium salt.—Crystallises from water in plates. (Found : Na, 9·8 ; $C_7H_4O_3BrNa$ requires Na, 9·6 per cent.)

Potassium salt.—Crystallises from water in plates. (Found : K, 15·4 ; $C_7H_4O_3BrK$ requires K, 15·3 per cent.)

Ammonium salt.—Crystallises from water in golden yellow shining needles. (Found : equivalent, 231·3 ; $C_7H_7O_3NBr$ requires equivalent 233·0.)

Silver salt.—Difficultly soluble in water and crystallises from it in short needles. (Found : Ag, 33·45 ; $C_7H_4O_3BrAg$ requires Ag, 33·30 per cent.)

Methyl-3-bromo-salicylate.—Obtained by treating the above silver salt (10 g.) with methyl iodide (excess) under reflux. It is extracted with hot acetone and distilled, b.p. 277°-278°/760 mm. (Found : Br, 35·1 ; $C_8H_7O_3Br$ requires Br, 34·6 per cent.)

3-Bromo-salicylamide.—Obtained by mechanically shaking a mixture of 3-bromo methyl salicylate (10 g.) and liquor ammonia (sp. gr. 0·88 ; 100 c.c.). It crystallises from alcohol in long needles, m.p. 162°–163°. (Found : Br, 36·95 ; $C_7H_6O_2NBr$ requires Br, 37·0 per cent.)

5-Bromo-2-methoxy-benzoic acid. —Method I : Bromine (10 g.) vapours were aspirated through an acetic acid solution of the methyl ether of salicylic acid (10 g.). The mixture was kept overnight and diluted to precipitate a solid which crystallised from alcohol in short needles, m.p. 118°–119° (Lit. 118°-119°).

Method II : 5-bromo-salicylic acid (25 g.) was dissolved in cold sodium hydroxide solution (50 c.c., 20 per cent.) and dimethyl sulphate (45 g.) was added 10 c.c. at a time, the bottle was tightly stoppered and allowed to come to room temperature before more dimethyl sulphate and alkali were added. It was then mechanically shaken for six hours and further refluxed for six hours. On acidification a solid was obtained which crystallised from alcohol in short needles, m.p. 118°–119°.

Sodium salt.—Crystallised from water in clusters of needles with three molecules of water. (Found : Na, 7·6 ; H_2O, 17·9 ; $C_8H_6O_3BrNa$, $3H_2O$ requires Na, 7·5 ; H_2O, 17·6 per cent.)

Potassium salt.—Crystallised from water in granules with four molecules of water. (Found : K, 11·5 ; H_2O, 21·11; $C_8H_6O_3BrK$, $4H_2O$ requires K, 11·4 ; H_2O, 21·10 per cent.)

Ethyl-5-bromo-2-methoxy-benzoate.—Obtained by alcoholysis at 100° or six hours, b.p. 295°/760 m.m. (Found : Br, 31·1 ; $C_{10}H_{11}O_3Br$ requires Br, 30·9 per cent.)

5-Bromo-2-methoxy-benzamide.—A mixture of 5-bromo-2-methoxy-benzoic acid (44 g.) and phosphorus pentachloride (60 g.) was heated at 100° until a clear liquid was obtained which was poured into an excess of strong ammonia.

The solid obtained was recrystallised from alcohol in flakes, m.p. 153°–154°. (Found : Br, 34·5 ; N, 6·0 ; $C_8H_8O_2N$ requires Br, 34·9 ; N, 6·1 per cent.)

3 : 5-*Dibromo*-2-*methoxy-benzoic acid.*—From dimethyl sulphate (3 mols.) 3 : 5-dibromo-salicylic acid (1 mol.) and sodium hydroxide (7 mols. 20 per cent.) as described for 5-bromo-2-methoxy-benzoic acid. The solid obtained after acidification, was crystallised from water in shining needles, m.p. 193°–194° (Lit. 193°–194°).

Sodium salt.—Crystallised from water in clusters of needles with $1\frac{1}{2}$ mols. of water. (Found : Na, 6·35 ; H_2O, 7·4 ; $C_8H_5O_3Br_2Na$, $1\frac{1}{2}H_2O$ requires Na, 6·4 ; H_2O, 7·5 per cent.)

Potassium salt.—Crystallised from water in granules with one molecule of water. (Found : K, 10·7 ; H_2O, 4·9 ; $C_8H_5O_3Br_2K$, H_2O requires K, 10·7 ; H_2O, 4·9 per cent.)

Calcium salt.—Crystallised from water in needles with six molecules of water. (Found : Ca, 5·2 ; H_2O, 14·3 ; $C_{16}H_{10}O_6Br_4Ca$, $6H_2O$ requires Ca, 5·2 ; H_2O, 14·1 per cent.)

Ethyl-3 : 5-*dibromo*-2-*methoxy-benzoate.*—Obtained by alcoholysis at 100° for six hours ; distils at 295°/760 mm. (Found : Br, 47·9 ; $C_{16}H_{10}O_3Br_2$ requires Br, 47·3 per cent.)

3 : 5-*Dibromo*-2-*methoxy-benzamide.*—Obtained by treating a mixture of 3 : 5-dibromo-2-methoxy-benzoic acid (30 g.) and phosphorus pentachloride (30 g.) as before for 5-bromo-2-methoxy-benzamide. It crystallises from alcohol in small yellow needles, m.p. 173°–174°. (Found : Br, 51·97 ; $C_8H_7O_2NBr_2$ requires Br, 51·8 per cent.)

3-*Bromo*-2-*methoxy-benzoic-acid.*—3-Bromo-salicylic acid (1 mol.), dimethyl sulphate (3 mols.) and sodium hydroxide (7 mols. 20 per cent.) when treated as for 5-bromo acid, yielded the required acid. It crystallised from benzene in plates, m.p. 134°–136° (Lit. 136°).

Potassium salt.—Crystallised from water in granules with one molecule of water. (Found : K, 13·9 ; H_2O, 6·3 ; $C_8H_6O_3BrK$, H_2O requires K, 13·6 ; H_2O, 6·3 per cent.)

Calcium salt.—Crystallised from water in feathery needles with $3\frac{1}{2}$ mols. of water. (Found : Ca, 7·1 ; H_2O, 11·2 ; $C_{16}H_{12}O_6Br_2Ca$, $3\frac{1}{2}H_2O$ requires Ca, 7·1 ; H_2O, 11·2 per cent.)

Barium salt.—Crystallised from water in short white needles with five molecules of water. (Found : Ba, 19·9 ; $C_{16}H_{12}O_6Br_2Ba$, $5H_2O$ requires Ba, 19·8 per cent.) As the compound decomposes on heating, the water of crystallisation could not be determined.

Ethyl-3-bromo-2-methoxy-benzoate.—By alcoholysis of the acid at 100° for six hours. It distils at 270°/760 m.m. (Found : Br, 31·2 ; $C_{10}H_{11}O_3Br$ requires Br, 30·9 per cent.)

3-*Bromo-2-methoxy-benzamide.*—Obtained by treating a mixture of the acid (1 mol.) and phosphorus pentachloride (excess over one mol.) as in the other two cases above. It crystallised from alcohol in flakes, m.p. 105°–106°. (Found : Br, 34·3 ; $C_8H_8O_2NBr$ requires Br, 34·8 per cent.)

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LATTICE-THEORY OF ALKALINE EARTH CARBONATES.

By B. Y. Oke.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received March 30, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

In four recent papers[1] referred to hereafter as I, II, III and IV the lattice-energies and the elasticity constants of the crystals of Calcite and Aragonite were calculated. This note is intended for the correction and modification of some of the results obtained in these papers.

The summations involved in I (2, 18) and III (1, 20) have been revised and extended till the denominators are equal to 200. With the revised values we obtain instead of I (2, 21) and III (1, 23)

$$\phi_0 = -e^2/b\ 149{\cdot}94, \quad \text{for Aragonite,} \qquad (1)$$

$$\phi_0 = -e^2/b\ 217{\cdot}52, \quad \text{for Calcite,} \qquad (2)$$

respectively.

Further results obtained from these values are given in Table I.

Table I.

Substance	M	ρ	a	$\frac{10^{-12}}{\chi}$	n	U
Calcite	100·07	2·71	90·26	0·658	8·59	610·7
				·719	9·30	616·9
				·746	9·61	619·1
Aragonite	100·07	2·93	56·81	·446	5·24	622·8
				·653	7·21	662·2
Strontianite	146·6	3·7	57·16	·574	7·63	633·5
Witherite	197·3	4·43	58·64	·495	7·50	612·6

The values of U are given in kilo-calories per gram molecule.

1. B. Y. Oke, *Proc. Ind. Acad. Sci.*, 1936, **4**, 1, 514, 525 and 667.

In the thermo-chemical cycle described in I, § 4, since CO_2 decomposes into carbon and molecular oxygen the multiplying factor 3/2 of D_0 is unnecessary ; hence instead of I (4, 2) we have the equation

$$Q_{MCO_3} - U_{MCO_3} + X + I_M - E_0 - Q_{CO_2} + S_M + D_0 = 0 \qquad (3)$$

X is the energy change of the reaction

$$(CO_3)^{--} = CO_2 + O^{--} \qquad (4)$$

Taking the lattice-energy values corresponding to the compressibility measurements of Madelung and Fuchs the values of X are calculated from (3) in Table II.

TABLE II.

	Calcite	Aragonite	Strontianite	Witherite
Q_{MCO_3}	231·8	270·8	279·2	283·0
I_M	413·0	413·0	383·9	349·1
$-E_0$	168·0	168·0	168·0	168·0
S_M	47·5	47·5	39·7	49·1
D_0	59·2	59·2	59·2	59·2
	919·5	958·5	930·6	908·4
U_{MCO_3}	619·7	662·8	634·3	613·4
Q_{CO_2}	97·0	97·0	97·0	97·0
	716·1	759·8	731·3	710·4
$-X$	203·4	198·7	198·7	198·0

All the values are given in kilo-calories.

The agreement between the different values is quite satisfactory ; though, of course, the closeness of the agreement, considering the inaccuracies in the compressibility measurements and the long summations involved is more a matter of chance.

The elasticity constants are determined with the revised values of a and for a series of values of n in the cases both of Calcite and Aragonite. The results obtained are given in Tables III and IV.

TABLE III. *Calcite.*

n	k	c_{33}^{θ}
8·5	0·608	$1·132 \times 10^{12}$
9·0	0·008	$1·156 \times 10^{12}$
9·5	−1·117	$1·179 \times 10^{12}$

These values agree well with the observed values given in IV (4, 10).

TABLE IV. *Aragonite.*

n	k	c_{33}^{θ}
5·0	1·89	$1·007 \times 10^{12}$
6·0	2·29	$1·021 \times 10^{12}$
7·0	2·59	$1·006 \times 10^{12}$

These values agree well with the observed values given in II (5, 2).

k which is defined in II (3, 2) as the the ratio of b_{kk} to $-b_{kk}'$ turns out to be different not only for the crystals of Calcite and Aragonite but in either case it varies with the value of the index of the repulsive potential. This is not surprising in view of the very simplified expression taken for the repulsive potential. In fact, as shown by Wasastjerna,[2] the attracting force between geometrically equivalent ions in the lattice deduced from the crystal properties is merely fictive, appearing in the calculations as a consequence in part of an incorrect assumption regarding the analytic form of the potential of repulsion and in part of the dependence on temperature of the elastic-constants having been disregarded. It cannot be claimed, therefore, that k has any physical bearing. It is of some interest, however, that with such a simple expression for repulsive potential, the calculated values of the elasticity-constants agree well with the observed values.

I wish to record how immensely I have benefited from the guidance and advice of Prof. Max Born during his stay at Bangalore, and I have to express my sincere thanks to the authorities of the Indian Institute of Science for the opportunity afforded me to carry out this work.

2. J. A. Wasastjerna, *Comm. Phy.-Math.*. (*Soc. Sci. Fennica*), **8**, No. 20.

THE PREPARATION OF ORTHO-PHTHALALDEHYDIC ACID.

By B. B. Dey and T. K. Srinivasan.

(*From the Department of Chemistry, Presidency College, Madras.*)

Received March 30, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Several methods for the preparation of this acid are described in literature.* Of these the methods described by Graebe and Trümpy (*loc. cit.*), Fuson (*loc. cit.*) and Gardner and Naylor (*loc. cit.*) appear to be more promising than the others. The starting material in all of these is naphthalene, the process being carried out in three steps, *viz.*, (*a*) the oxidation of naphthalene to phthalonic acid by a boiling solution of potassium permanganate, (*b*) the conversion of the phthalonic acid into either its anil or into the sodium bisulphite addition compound, and (*c*) the hydrolytic decomposition of the anil or the sodium bisulphite compound into phthalaldehydic acid.

The preparation of phthalaldehydic acid, large quantities of which were required in connection with certain investigations in the *iso*quinoline series, was carried out at first by Fuson's method *viâ* the anil of phthalonic acid, and later by the methods of Graebe and Trümpy (*loc. cit.*) and of Gardner and Naylor (*loc. cit.*) *viâ* the sodium bisulphite addition product. The latter method was found to be decidedly superior to that of Fuson. The yields of phthalaldehydic acid, however, were found to be very variable, and after several careful repetitions of the process, the discrepancies in the results were found to proceed almost entirely from rather incomplete directions given by the previous workers regarding the method of decomposition of the bisulphite compound by treatment with hydrochloric acid. Wegscheider and Bondi (*loc. cit.*) had found it necessary to heat the bisulphite compound on

* Coulson and Gautier, *Bull. Soc. Chim.*, 1886, **45** (2), 507.
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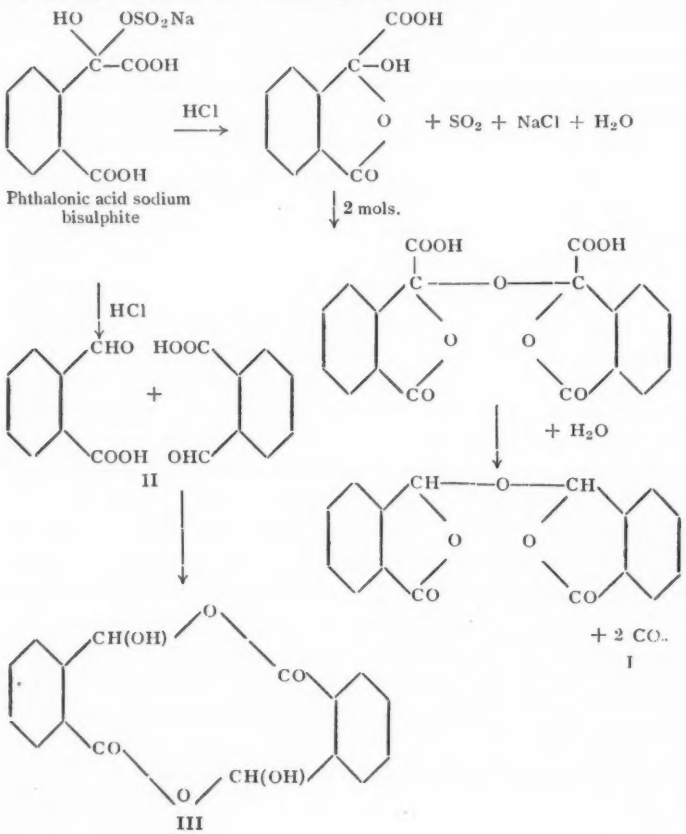
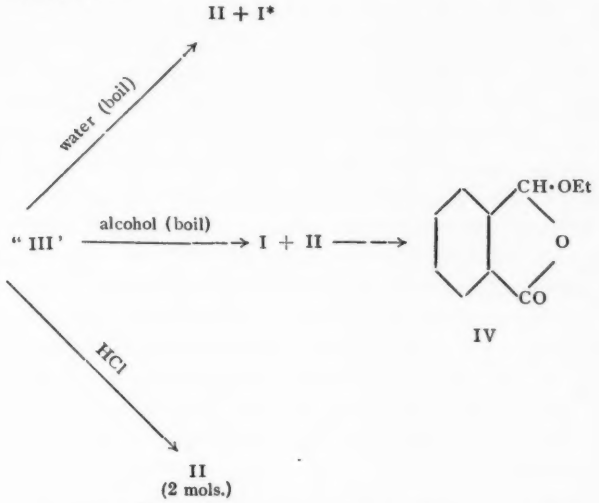
Gardner and Naylor, Jr., *Organic Syntheses*, 1936, **16**, 68.

the water-bath for *several days* with a large excess of hydrochloric acid, whereas Gardner and Naylor recommended treatment with concentrated hydrochloric acid and evaporation to dryness twice on the steam-bath as sufficient. Several interesting observations have now been made which have led to a clearer understanding of this stage of the process and to the introduction of certain modifications which have ensured satisfactorily consistent yields of the product. In the first place, it was noticed that the decomposition of the sodium bisulphite compound by means of concentrated hydrochloric acid was by no means so simple a process as that represented by the previous workers. The product formed on evaporating twice the phthalonic acid sodium bisulphite with hydrochloric acid to dryness at 100° has been found to be a mixture of diphthalide ether (I) (Graebe and Trümpy, *loc. cit.*) and another compound to which the constitution " III " has been assigned provisionally, the reactions being expressed by the scheme given below :—



These two compounds are easily separated by boiling benzene (Soxhlet): "III" goes into solution and the diphthalide ether, which is practically insoluble, is left behind along with the sodium chloride which could be subsequently washed out with water.

On boiling "III" with water alone for some time it was converted mostly into phthalaldehydic acid and a small amount of diphthalide ether, while with boiling alcohol, it broke up into a mixture of diphthalide ether and the ethyl ester of pseudo-phthalaldehydic acid (IV). It was however hydrolysed quantitatively to phthalaldehydic acid by boiling vigorously with excess of concentrated hydrochloric acid. These decompositions can be readily understood and explained in terms of the structure III assigned to the product as follows:—



Further, the diphthalide ether (I) was readily converted into phthalaldehydic acid (II) by boiling 2N aqueous caustic soda.

In the preparation of phthalaldehydic acid, therefore, after working up the benzene extract in the manner described by Gardner and Naylor (*Organic Syntheses*, 1936, **16**, p. 69), the residue in the extractor should be washed with water to remove the sodium chloride and then boiled with glacial acetic acid to recover the diphthalide ether, the latter being subsequently converted into phthalaldehydic acid by hot alkali. The dry

* Diphthalide ether (I) itself has been observed to decompose *slowly* in boiling water yielding phthalaldehydic acid.

residue obtained by evaporation of the benzene solution should also be boiled once more with about six times its weight of concentrated hydrochloric acid for half an hour and the solution slightly diluted and cooled in ice. A total yield of 9 grams (77 per cent. of the theoretical amount) was uniformly obtained in this way from 15 grams of phthalonic acid. The latter has been obtained under the conditions described in this paper in a yield of 16 to 18 grams from 20 grams of Naphthalene.

Experimental.

The oxidation of naphthalene to phthalonic acid.—In a 2-litre round bottom flask fitted with a reflux condenser, are placed naphthalene (20 g.), potassium permanganate (130 g.) and water (1·6 litres). The mixture is heated on wire-gauze to vigorous boiling for 4 hours, cooled and filtered from the manganese hydrate and the unreacted naphthalene which weighs usually 4 to 5 g. The filtrate is evaporated to 100 c.c. on the steam-bath, cooled in ice and acidified with ice-cold concentrated sulphuric acid (25 c.c.). The solution is once again evaporated till the residue is only slightly moist. The moist residue which contains potassium sulphate and phthalonic acid, is taken in a 500 c.c. separating funnel and extracted 4 times with ether (30 c.c. at a time). The ether is distilled on a water-bath and the oil left behind is transferred to a dish and heated for an hour on the steam-bath. On cooling and rubbing, the oil solidifies to a hard mass. This solid which contains phthalonic acid mixed with some phthalic acid is stirred with cold water (60 c.c.) for a few minutes and filtered. The filtrate containing phthalonic acid is evaporated on the steam-bath and the residue of thick colourless oil left overnight in vacuum over sulphuric acid when it solidifies to a hard mass, m.p. 115° with softening at 80°. Yield, 16–18 g, *i.e.*, after allowing for the naphthalene recovered, the yield is 75 per cent. of the theoretical amount.

Method I.

Preparation of phthalaldehydic acid via *phthalonic acid sodium bisulphite.*

Sodium bisulphite derivative of phthalonic acid.—The crude phthalonic acid (15 g.) is dissolved in water (60 c.c.) and treated with a solution of sodium bisulphite prepared by saturating sodium bicarbonate (30 g.) in 250 c.c. water with sulphur dioxide. The mixture is evaporated completely to dryness on the steam-bath.

Decomposition of phthalonic acid sodium bisulphite with concentrated hydrochloric acid. Formation of the dimolecular compound "III" and of diphthalide ether.—To the whole of the dry sodium bisulphite derivative prepared above, concentrated hydrochloric acid (40 c.c.) is added with stirring

and the mixture evaporated to dryness on the steam-bath. This treatment with another 40 c.c. hydrochloric acid and subsequent evaporation to dryness are repeated. The residue is thoroughly dried in vacuum over concentrated H_2SO_4 and then extracted with dry benzene in a Soxhlet apparatus using a thimble, 4″ by 1″. The benzene is removed by distillation and the thick colourless oil which solidifies on rubbing with a small quantity of petroleum ether is crystallised from warm benzene. It formed plates which melted to an opaque wax-like liquid at 98° and became perfectly clear at 168°. Yield, 7–8 g. 0·03180 g. gave 0·07403 g. CO_2 and 0·01148 g. H_2O. [Found : C, 63·49 ; H, 4·012 ; $C_{16}H_{12}O_6$ requires C, 64·0, H, 4·0 per cent.]

0·4506 g. dissolved in 28·5742 g. of benzene, elevated the boiling point by 0·16°.

[Found : Mol. wt., 257·2 ; $C_{16}H_{12}O_6$ requires M.W., 300].

Action of boiling water on " III ".—The compound (8 g.) is made into a thin cream with water (80 c.c.) and heated on the wire-gauze to boiling for twenty minutes. The bulk of the solid slowly goes into solution leaving behind only a small amount of a residue which is filtered. The filtrate is concentrated to about 20 c.c. on the steam-bath and cooled. Phthalaldehydic acid separates out in white flaky crystals, m.p. 96°. Yield, 6 g. The mother-liquor, on complete evaporation, yields a further 0·5 g. of the acid. The undissolved residue crystallises from glacial acetic acid in colourless needles, m.p. 222° not depressed by admixture with diphthalide ether (*vide infra*). Yield, 1 g.

Action of boiling alcohol on " III ".—The compound (1 g.) is boiled with 40 c.c. alcohol till it goes into solution. On cooling, beautiful colourless needles, m.p. 222°, are deposited. Yield, 0·4 g. This was identified with diphthalide ether prepared by heating phthalaldehydic acid to 240–250° (Graebe and Trümpy, *loc. cit.*).

0·1224 g. gave 0·03056 g. CO_2 and 0·00434 g. H_2O.

[Found : C, 68·10 ; H, 3·94 ; $C_{16}H_{10}O_5$ requires C, 68·08 ; H, 3·54 per cent.]

The mother-liquor, on spontaneous evaporation, left behind an oil which slowly solidified. Crystallisation from dilute alcohol gave needles, m.p. 65°. Yield, 0·5 g. This was identified as the ethyl ester of pseudo-phthalaldehydic acid by a mixed melting point.

Action of caustic soda on the diphthalide ether, m.p. 222°.—The substance (0·4 g.) is boiled with 2N NaOH (10 c.c.) till it goes into solution. On cooling and acidifying with dilute HCl, phthalaldehydic acid slowly separates out in crystals, m.p. 96°. Yield, 0·3 g.

Nitration of " III ".—1 g. is dissolved in concentrated sulphuric acid (7 c.c.), cooled to 0° and treated with a solution of potassium nitrate (0·7 g.) in the same acid (1 c.c.). After standing for an hour at the laboratory temperature, the solution is poured on to 25 g. crushed ice and the separating solid is filtered, washed and dried. It was found to be rather impure, two crystallisations from alcohol and one from acetic acid giving a crystalline solid melting indefinitely between 120° and 140°. Yield, 0·7 g.

Hydrolysis of the crude nitro-derivative to 3-nitro-phthalaldehydic acid.—0·6 g. of the nitrobody was boiled with concentrated HCl (4 c.c.) for about 15 minutes and the hot solution filtered. On cooling, lemon-yellow hard prisms (m.p. 157°) separated out. These melted at the same temperature when mixed with an authentic specimen of 3-nitro-phthalaldehydic acid.

Hydrolysis of " III " with boiling HCl. Formation of phthalaldehydic acid.—The compound (8 g.) is made into a thin cream with concentrated HCl (40 c.c.) and boiled on the wire-gauze. The substance goes gradually into solution. After about half an hour's vigorous boiling the hot solution is diluted with water (15 c.c.) and filtered. The filtrate, on cooling, deposited light-yellow plates, m.p. 96°. Yield, 7·5 g. A small quantity was crystallised from chloroform ; colourless plates, m.p. 100°.

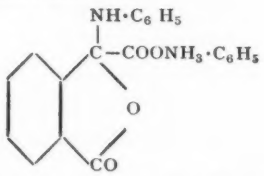
The diphthalide ether.—The residue left in the thimble after extraction with benzene is stirred up twice with water and filtered. The insoluble crystalline residue dissolved in hot glacial acetic acid from which it separated as soft colourless needles, m.p. 222°. Yield, 2·3 g.

1·7 g. of phthalaldehydic acid was obtained by boiling the phthalide ether (2·3 g.) with 2N caustic soda in the manner described before.

Mehod II.

Preparation of phthalaldehydic acid via *phthalonic acid-anil* (*Fuson*, loc. cit.).

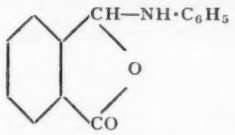
Aniline salt of phthalonic acid-anil.



Phthalonic acid (5 g.) is dissolved in water (10 c.c.) and freshly distilled aniline (10 c.c.) is added and the mixture heated on the water-bath for about 20 minutes and rubbed continuously. A mass of light colourless crystals of the aniline salt of the anil was formed, m. p. 165°. Yield, 8 g.

Fuson's method of treatment of the phthalonic acid in acid (HCl) solution with aniline is defective and gives a much poorer yield of the anil. It is essential for getting the yield given above to isolate the phthalonic acid and to have no free mineral acids present during the treatment with aniline.

Decomposition of the aniline salt to anilidophthalide.—



The salt (5 g.) is dried at 100° for 2 hours, suspended in xylene dried over sodium (50 c.c.) and heated on a sand-bath with an air condenser carrying a $CaCl_2$ drying tube, for half an hour. The bright crimson red solution, on cooling, deposited a quantity of cream coloured sandy crystals which were filtered and dried, m.p. 174°. Yield, 3 g.

Phthalaldehydic acid.—The anilidophthalide (3 g.) and 10 per cent. hydrochloric acid (30 c.c.) are boiled together for 30 minutes on wire-gauze, filtered and concentrated to a small bulk. On cooling, colourless flakes separated out, m.p. 96°. Yield, 0·8 g.

DIFFERENTIAL INVARIANTS FOR PATH SPACES OF ORDER 3.*

By V. Seetharaman, B.Sc. (Hons.),
Research Scholar, Annamalai University.

Received March 30, 1937.
(Communicated by Prof. A. Narasinga Rao.)

Following the methods of Prof. Kosambi,§ which I briefly recapitulate here, I calculate in this note, the differential invariants for a space of paths, where the paths are defined by the differential equations of order 4, *viz.*,

$$x^{(4)i} + a^i\,(x,\ x^{(1)},\ x^{(2)},\ x^{(3)},\ t) = 0. \tag{1}$$

The equations of variation of (1) expressed in the tensorial form

$$\mathrm{D}^{(4)}\,u^i + \underset{\gamma}{\mathrm{P}}{}^i_r\,(\mathrm{D}^\gamma\,u^r) = 0 \qquad (\gamma = 0,\ 1,\ 2,\ 3) \tag{2}$$

define the various 'curvature tensors' $\underset{\gamma}{\mathrm{P}}{}^i_r$. To get at an intrinsic connection we put $\underset{3}{\mathrm{P}}{}^i_r \equiv a^i_{(3)r} - 4\gamma^i_r = 0$ thus defining $\gamma^i_r = \frac{1}{4}a^i_{(3)r}$.

The equations of the paths (1) are expressed in the invariant form

$$(\mathrm{D}^3\,x^{(1)i}) + \tfrac{1}{2}\,\underset{2}{\mathrm{P}}{}^i_r\,(\mathrm{D}x^{(1)r}) + \tfrac{1}{4}\,\underset{1}{\mathrm{P}}{}^i_r\,x^{(1)r} + \epsilon^i = 0 \tag{3}$$

where

$$\epsilon^i = a^i - \tfrac{1}{4}\,a^i_{(1)r}\,x^{(1)r} - \tfrac{1}{2}\,a^i_{(2)r}\,x^{(2)r} - \tfrac{3}{4}\,a^i_{(3)r}\,x^{(3)r} \tag{4}$$

are the components of a vector.

Besides the three fundamental differential operators given by

$$\mathrm{D}u^i = u^{(1)i} + \gamma^i_r\,u^r,\ \underset{3}{\nabla}_r = \frac{\partial}{\partial x^{(3)r}},\ \text{and}\ \frac{\partial}{\partial t} \tag{5}$$

we get, on alternating the first two successively and omitting terms that are tensors, three more differential operators $\underset{2}{\nabla}_r$, $\underset{1}{\nabla}_r$ and $\underset{0}{\nabla}_r$.

The differential invariants are got by alternating all these differential operations taken two at a time. The following is the result of that operation,

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* This note and the previous one on path spaces of order 2 (*Proc. Ind. Acad. Sci.*, 1937, 5, No. 2) are undertaken as a preliminary to the calculation of invariants for path spaces of order σ, under the suggestion of Prof. Kosambi, for which I am deeply indebted to him.

§ D. D. Kosambi, *Quar. Jour. of Math.*, 1936, 7, No. 26.

$$(6)\qquad [\underset{3}{\nabla}_k \underset{3}{\nabla}_j u^i - \underset{3}{\nabla}_j \underset{3}{\nabla}_k u^i] = 0$$

$$(7)\qquad \left[\frac{\partial}{\partial t}(\underset{3}{\nabla}_k u^i) - \underset{3}{\nabla}_k \left(\frac{\partial u^i}{\partial t}\right)\right] = 0$$

$$(8)\qquad [\underset{3}{\nabla}_k \underset{2}{\nabla}_j u^i - \underset{2}{\nabla}_j \underset{3}{\nabla}_k u^i] = -3 \underset{3}{\nabla}_r u^i [\gamma^r_{j(3)k}].$$

$$(9)\qquad [\underset{3}{\nabla}_k \underset{1}{\nabla}_j u^i - \underset{1}{\nabla}_j \underset{3}{\nabla}_k u^i]$$
$$= -2 \underset{2}{\nabla}_r u^i [\gamma^r_{j(3)k}] - \tfrac{1}{2} \underset{3}{\nabla}_r u^i [\underset{2}{\mathrm{P}}{}^r_{j(3)k} + 4 \underset{2}{\nabla}_j \gamma^r_k]$$

$$(10)\qquad [\underset{3}{\nabla}_k \underset{0}{\nabla}_j u^i - \underset{0}{\nabla}_j \underset{3}{\nabla}_k u^i]$$
$$= u^r [\underset{3}{\nabla}_k \underset{1}{\nabla}_j \gamma^i_r] - \underset{1}{\nabla}_r u^i [\gamma^r_{j(3)k}]$$
$$- \tfrac{1}{6} \underset{2}{\nabla}_r u^i [5 \underset{2}{\mathrm{P}}{}^r_{j(3)k} + 4 \underset{2}{\nabla}_j \gamma^r_k]$$
$$+ \tfrac{1}{2} \underset{3}{\nabla}_r u^i [\underset{2}{\nabla}_k \underset{2}{\mathrm{P}}{}^r_j + \underset{2}{\nabla}_j \underset{2}{\mathrm{P}}{}^r_k + \mathrm{D} \underset{3}{\nabla}_k \underset{2}{\mathrm{P}}{}^r_j + 10\, \mathrm{D} \underset{2}{\nabla}_j \gamma^r_k].$$

$$(11)\qquad [\underset{2}{\nabla}_k \underset{2}{\nabla}_j u^i - \underset{2}{\nabla}_j \underset{2}{\nabla}_k u^i] = 3 \underset{3}{\nabla}_r u^i [\underset{32}{\mathrm{R}}{}^r_{jk}]$$

where

$$(11a)\qquad \underset{32}{\mathrm{R}}{}^r_{jk} = \tfrac{1}{10} (\underset{3}{\nabla}_k \underset{2}{\mathrm{P}}{}^r_j - \underset{3}{\nabla}_j \underset{2}{\mathrm{P}}{}^r_k)$$

$$(12)\qquad [\underset{2}{\nabla}_k \underset{1}{\nabla}_j u^i - \underset{1}{\nabla}_j \underset{2}{\nabla}_k u^i]$$
$$= -2 \underset{2}{\nabla}_r u^i [\underset{2}{\nabla}_k \gamma^r_j] - \tfrac{1}{2} \underset{3}{\nabla}_r u^i [\underset{2}{\nabla}_k \underset{2}{\mathrm{P}}{}^r_j + \underset{2}{\nabla}_j \underset{2}{\mathrm{P}}{}^r_k + 6\, \mathrm{D} \underset{2}{\nabla}_j \gamma^r_k].$$

$$(13)\qquad [\underset{2}{\nabla}_k \underset{0}{\nabla}_j u^i - \underset{0}{\nabla}_j \underset{2}{\nabla}_k u^i]$$
$$= u^r [\underset{2}{\nabla}_k \underset{1}{\nabla}_j \gamma^i_r] - \underset{1}{\nabla}_r u^i [\underset{2}{\nabla}_k \gamma^r_j]$$
$$- \underset{2}{\nabla}_r u^i [\underset{2}{\nabla}_k \underset{2}{\mathrm{P}}{}^r_j - \underset{22}{\mathrm{R}}{}^r_{jk} + \mathrm{D} \underset{2}{\nabla}_j \gamma^r_k]$$
$$+ \underset{3}{\nabla}_r u^i [7 \underset{12}{\mathrm{R}}{}^r_{jk} - 3 \underset{21}{\mathrm{R}}{}^r_{jk} + \mathrm{D} \underset{2}{\nabla}_k \underset{2}{\mathrm{P}}{}^r_j - \tfrac{2}{5} \mathrm{D} \underset{22}{\mathrm{R}}{}^r_{jk} + 3\, \mathrm{D}^2 \underset{2}{\nabla}_j \gamma^r_k$$
$$+ \tfrac{3}{5} \underset{2}{\mathrm{P}}{}^r_l \underset{32}{\mathrm{R}}{}^l_{jk} + \tfrac{6}{5} (\underset{2}{\nabla}_k \gamma^r_l) \underset{2}{\mathrm{P}}{}^l_j - \tfrac{6}{5} (\underset{2}{\nabla}_j \gamma^r_l) \underset{2}{\mathrm{P}}{}^l_k]$$

where

$$(13a)\qquad \underset{12}{\mathrm{R}}{}^i_{jk} = \tfrac{1}{10} (\underset{1}{\nabla}_k \underset{2}{\mathrm{P}}{}^i_j - \underset{1}{\nabla}_j \underset{2}{\mathrm{P}}{}^i_k)$$

$$(13b)\qquad \underset{21}{\mathrm{R}}{}^i_{jk} = \tfrac{1}{10} (\underset{2}{\nabla}_k \underset{1}{\mathrm{P}}{}^i_j - \underset{2}{\nabla}_j \underset{1}{\mathrm{P}}{}^i_k)$$

$$(13c)\qquad \underset{22}{\mathrm{R}}{}^i_{jk} = \tfrac{1}{6} (\underset{2}{\nabla}_k \underset{2}{\mathrm{P}}{}^i_j - \underset{2}{\nabla}_j \underset{2}{\mathrm{P}}{}^i_k).$$

$$(14)\quad [\underset{1}{\nabla}_k \underset{1}{\nabla}_j u^i - \underset{1}{\nabla}_j \underset{1}{\nabla}_k u^i] = 2 \underset{2}{\nabla}_r u^i [\underset{22}{R}{}^r_{jk} - D \underset{32}{R}{}^r_{jk}]$$
$$- \underset{3}{\nabla}_r u^i [7 \underset{12}{R}{}^r_{jk} - 3 \underset{21}{R}{}^r_{jk} + \tfrac{6}{5} D \underset{22}{R}{}^r_{jk} + \tfrac{3}{5} \underset{2}{P}{}^r_l \underset{32}{R}{}^l_{jk}$$
$$+ \tfrac{6}{5} (\underset{2}{\nabla}_k \gamma^r_l) \underset{2}{P}{}^l_j - \tfrac{6}{5} (\underset{2}{\nabla}_j \gamma^r_l) \underset{2}{P}{}^l_k].$$

$$(15)\quad [\underset{1}{\nabla}_k \underset{0}{\nabla}_j u^i - \underset{0}{\nabla}_j \underset{1}{\nabla}_k u^i]$$
$$= u^r [\underset{1}{\nabla}_k \underset{1}{\nabla}_j \gamma^i_r] + \underset{1}{\nabla}_r u^i [\underset{22}{R}{}^r_{jk} - D \underset{32}{R}{}^r_{jk}]$$
$$- \underset{2}{\nabla}_r u^i [\underset{21}{R}{}^r_{jk} - 4 \underset{12}{R}{}^r_{jk} + \tfrac{8}{5} D \underset{22}{R}{}^r_{jk} + \tfrac{3}{2} \underset{1}{\nabla}_k \underset{2}{P}{}^r_j - \tfrac{1}{2} \underset{2}{\nabla}_k \underset{1}{P}{}^r_j$$
$$- \tfrac{1}{5} \underset{2}{P}{}^r_l \underset{32}{R}{}^l_{jk} - \underset{2}{P}{}^r_l (\underset{2}{\nabla}_k \gamma^l_j) + \tfrac{2}{5} (\underset{2}{\nabla}_j \gamma^r_l) \underset{2}{P}{}^l_k$$
$$+ \tfrac{8}{5} (\underset{2}{\nabla}_k \gamma^r_l) \underset{2}{P}{}^l_j - 2 D^2 \underset{2}{\nabla}_j \gamma^r_k]$$
$$+ \underset{3}{\nabla}_r u^i \Big[\underset{0}{\nabla}_j \underset{2}{P}{}^r_k + \underset{0}{\nabla}_k \underset{2}{P}{}^r_j + D \underset{1}{\nabla}_k \underset{2}{P}{}^r_j + \tfrac{1}{2} D \underset{2}{\nabla}_k \underset{1}{P}{}^r_j - \underset{1}{\nabla}_k \underset{1}{P}{}^r_j$$
$$- 3D^2 \underset{22}{R}{}^r_{jk} + 3D^3 \underset{32}{R}{}^r_{jk} - \tfrac{1}{2} D \underset{1}{\nabla}_j \underset{2}{P}{}^r_k + 2D^3 \underset{2}{\nabla}_k \gamma^r_j$$
$$- 3 \underset{2}{P}{}^l_j (\underset{22}{R}{}^r_{lk} - D \underset{32}{R}{}^r_{lk}) + \underset{2}{P}{}^l_k (\underset{22}{R}{}^r_{lj} - D \underset{32}{R}{}^r_{lj})$$
$$+ \underset{2}{P}{}^r_l (\underset{22}{R}{}^l_{jk} - D \underset{32}{R}{}^l_{jk}) + 3 (\underset{2}{\nabla}_l \gamma^r_k) (2D \underset{2}{P}{}^l_j - \underset{1}{P}{}^l_j)$$
$$- 3 \gamma^r_{k(3)l} (D^2 \underset{2}{P}{}^l_j - D \underset{1}{P}{}^l_j + \underset{0}{P}{}^l_j) - (\underset{2}{\nabla}_l \gamma^r_j) (2D \underset{2}{P}{}^l_k - \underset{1}{P}{}^l_k)$$
$$+ \gamma^r_{j(3)l} (D^2 \underset{2}{P}{}^l_k - D \underset{1}{P}{}^l_k + \underset{0}{P}{}^l_k) + D (\underset{2}{P}{}^r_l \underset{2}{\nabla}_k \gamma^l_j)$$
$$- 2D (\underset{2}{P}{}^l_j \underset{2}{\nabla}_k \gamma^r_l) \Big].$$

$$(16)\quad [\underset{0}{\nabla}_k \underset{0}{\nabla}_j u^i - \underset{0}{\nabla}_j \underset{0}{\nabla}_k u^i]$$
$$= u^r [\tfrac{1}{12} (\underset{1}{\nabla}_j \underset{}{A}{}^i_{rk} - \underset{1}{\nabla}_k \underset{}{A}{}^i_{rj}) + D (\underset{1}{\nabla}_j \underset{1}{\nabla}_k \gamma^i_r - \underset{1}{\nabla}_k \underset{1}{\nabla}_j \gamma^i_r)$$
$$+ (\underset{22}{R}{}^l_{jk} - D \underset{32}{R}{}^l_{jk}) (\tfrac{1}{6} \underset{2}{\nabla}_l \underset{2}{P}{}^i_r + D \underset{2}{\nabla}_l \gamma^i_r)$$
$$+ \underset{2}{\nabla}_r \gamma^i_l \{\underset{21}{R}{}^l_{jk} - \tfrac{7}{5} \underset{12}{R}{}^l_{jk} - \tfrac{2}{5} D \underset{22}{R}{}^l_{jk} - \tfrac{1}{5} \underset{2}{P}{}^l_m \underset{32}{R}{}^m_{jk}$$
$$- \tfrac{2}{5} (\underset{2}{\nabla}_k \gamma^l_m) \underset{2}{P}{}^m_j + \tfrac{2}{5} (\underset{2}{\nabla}_j \gamma^l_m) \underset{2}{P}{}^m_k\}]$$
$$+ \underset{0}{\nabla}_r u^i [\underset{22}{R}{}^r_{jk} - D \underset{32}{R}{}^r_{jk}]$$
$$+ \underset{1}{\nabla}_r u^i [\underset{21}{R}{}^r_{jk} + \underset{12}{R}{}^r_{jk} - \tfrac{7}{5} D \underset{22}{R}{}^r_{jk} + D^2 \underset{32}{R}{}^r_{jk} - \tfrac{1}{5} \underset{2}{P}{}^r_l \underset{32}{R}{}^l_{jk}$$
$$- \tfrac{2}{5} (\underset{2}{\nabla}_k \gamma^r_l) \underset{2}{P}{}^l_j + \tfrac{2}{5} (\underset{2}{\nabla}_j \gamma^r_l) \underset{2}{P}{}^l_k]$$

$$
\begin{aligned}
&+ \underset{2}{\nabla}_r u^i \Big[\underset{11}{R}{}^r_{jk} - \underset{02}{R}{}^r_{jk} - \tfrac{1}{2} D^2 \underset{22}{R}{}^r_{jk} + \tfrac{1}{2} D^3 \underset{32}{R}{}^r_{jk} + \tfrac{3}{4} \underset{2}{P}{}^r_l \left(\underset{22}{R}{}^l_{jk} - D \underset{32}{R}{}^l_{jk} \right) \\
&\quad + \tfrac{1}{2} \underset{2}{P}{}^l_k \left(\underset{22}{R}{}^r_{lj} - D \underset{32}{R}{}^r_{lj} \right) - \tfrac{1}{2} \underset{2}{P}{}^l_j \left(\underset{22}{R}{}^r_{lk} - D \underset{32}{R}{}^r_{lk} \right) \\
&\quad - \tfrac{1}{2} \underset{2}{\nabla}_l \gamma^r_j \left(2D \underset{2}{P}{}^l_k - \underset{1}{P}{}^l_k \right) + \tfrac{1}{2} \gamma^r_{j(3)l} \left(D^2 \underset{2}{P}{}^l_k - D \underset{1}{P}{}^l_k + \underset{0}{P}{}^l_k \right) \\
&\quad + \tfrac{1}{2} \underset{2}{\nabla}_l \gamma^r_k \left(2D \underset{2}{P}{}^l_j - \underset{1}{P}{}^l_j \right) - \tfrac{1}{2} \gamma^r_{k(3)l} \left(D^2 \underset{2}{P}{}^l_j - D \underset{1}{P}{}^l_j + \underset{0}{P}{}^l_j \right) \Big] \\
&+ \underset{3}{\nabla}_r u^i \Big[- \underset{01}{R}{}^r_{jk} + D \underset{02}{R}{}^r_{jk} + D \underset{11}{R}{}^r_{jk} - \tfrac{1}{2} D^3 \underset{22}{R}{}^r_{jk} + \tfrac{1}{2} D^4 \underset{32}{R}{}^r_{jk} \\
&\quad + \underset{1}{P}{}^r_l \left(\underset{22}{R}{}^l_{jk} - D \underset{32}{R}{}^l_{jk} \right) + \underset{1}{P}{}^l_j \left(\underset{22}{R}{}^r_{kl} - D \underset{32}{R}{}^r_{kl} \right) - \underset{1}{P}{}^l_k \left(\underset{22}{R}{}^r_{jl} - D \underset{32}{R}{}^r_{jl} \right) \\
&\quad - \tfrac{5}{4} D \{ \underset{2}{P}{}^r_l \left(\underset{22}{R}{}^l_{jk} - D \underset{32}{R}{}^l_{jk} \right) \} + \tfrac{3}{2} D \{ \underset{2}{P}{}^l_k \left(\underset{22}{R}{}^r_{jl} - D \underset{32}{R}{}^r_{jl} \right) \} \\
&\quad - \tfrac{3}{2} D \{ \underset{2}{P}{}^l_j \left(\underset{22}{R}{}^r_{kl} - D \underset{32}{R}{}^r_{kl} \right) \} \\
&\quad + \tfrac{1}{2} D \{ \gamma^r_{j(3)l} \left(D^2 \underset{2}{P}{}^l_k - D \underset{1}{P}{}^l_k + \underset{0}{P}{}^l_k \right) \} - \tfrac{1}{2} D \{ \gamma^r_{k(3)l} \left(D^2 \underset{2}{P}{}^l_j - D \underset{1}{P}{}^l_j + \underset{0}{P}{}^l_j \right) \} \\
&\quad + \left(\underset{2}{P}{}^r_{k(3)l} - D \gamma^r_{k(3)l} \right) \left(D^2 \underset{2}{P}{}^l_j - D \underset{1}{P}{}^l_j + \underset{0}{P}{}^l_j \right) \\
&\quad - \left(\underset{2}{P}{}^r_{j(3)l} - D \gamma^r_{j(3)l} \right) \left(D^2 \underset{2}{P}{}^l_k - D \underset{1}{P}{}^l_k + \underset{0}{P}{}^l_k \right) \\
&\quad + \left(\underset{2}{\nabla}_l \underset{2}{P}{}^r_j - \tfrac{3}{2} D \underset{2}{\nabla}_l \gamma^r_j \right) \left(2D \underset{2}{P}{}^l_k - \underset{1}{P}{}^l_k \right) \\
&\quad - \left(\underset{2}{\nabla}_l \underset{2}{P}{}^r_k - \tfrac{3}{2} D \underset{2}{\nabla}_l \gamma^r_k \right) \left(2D \underset{2}{P}{}^l_j - \underset{1}{P}{}^l_j \right) \\
&\quad - \underset{2}{\nabla}_l \gamma^r_j \left(\tfrac{1}{2} D \underset{1}{P}{}^l_k - \underset{0}{P}{}^l_k \right) + \underset{2}{\nabla}_l \gamma^r_k \left(\tfrac{1}{2} D \underset{1}{P}{}^l_j - \underset{0}{P}{}^l_j \right) \\
&\quad + 2 \underset{2}{P}{}^r_l \{ \underset{12}{R}{}^l_{jk} + \underset{21}{R}{}^l_{jk} - \tfrac{7}{5} D \underset{22}{R}{}^l_{jk} + D^2 \underset{32}{R}{}^l_{jk} - \tfrac{1}{5} \underset{2}{P}{}^l_m \underset{32}{R}{}^m_{jk} \\
&\qquad - \tfrac{2}{5} \left(\underset{2}{\nabla}_k \gamma^l_m \right) \underset{2}{P}{}^m_j + \tfrac{2}{5} \left(\underset{2}{\nabla}_j \gamma^l_m \right) \underset{2}{P}{}^m_k \} \\
&\quad + 4 \underset{2}{P}{}^l_j \{ - \underset{12}{R}{}^r_{lk} - \underset{21}{R}{}^r_{lk} + \tfrac{7}{5} D \underset{22}{R}{}^r_{lk} - D^2 \underset{32}{R}{}^r_{lk} + \tfrac{1}{5} \underset{2}{P}{}^r_m \underset{32}{R}{}^m_{lk} \\
&\qquad + \tfrac{2}{5} \left(\underset{2}{\nabla}_k \gamma^r_m \right) \underset{2}{P}{}^m_l - \tfrac{2}{5} \left(\underset{2}{\nabla}_l \gamma^r_m \right) \underset{2}{P}{}^m_k + \tfrac{1}{8} \underset{1}{\nabla}_l \underset{2}{P}{}^r_k + \tfrac{1}{8} A^r_{kl} \} \\
&\quad - 4 \underset{2}{P}{}^l_k \{ - \underset{12}{R}{}^r_{lj} - \underset{21}{R}{}^r_{lj} + \tfrac{7}{5} D \underset{22}{R}{}^r_{lj} - D^2 \underset{32}{R}{}^r_{lj} + \tfrac{1}{5} \underset{2}{P}{}^r_m \underset{32}{R}{}^m_{lj} \\
&\qquad + \tfrac{2}{5} \left(\underset{2}{\nabla}_j \gamma^r_m \right) \underset{2}{P}{}^m_l - \tfrac{2}{5} \left(\underset{2}{\nabla}_l \gamma^r_m \right) \underset{2}{P}{}^m_j + \tfrac{1}{8} \underset{1}{\nabla}_l \underset{2}{P}{}^r_j + \tfrac{1}{8} A^r_{jl} \} \Big]
\end{aligned}
$$

where

$$(16a) \qquad \underset{02}{R}{}^r_{jk} = \underset{0}{\nabla}_k \underset{2}{P}{}^r_j - \underset{0}{\nabla}_j \underset{2}{P}{}^r_k$$

$$(16b) \qquad \underset{01}{R}{}^r_{jk} = \underset{0}{\nabla}_k \underset{1}{P}{}^r_j - \underset{0}{\nabla}_j \underset{1}{P}{}^r_k$$

$$(16c)\quad \underset{11}{R}{}^{r}_{jk} = \tfrac{1}{6}\left(\underset{1}{\nabla}_k \underset{1}{P}{}^{r}_{j} - \underset{1}{\nabla}_j \underset{1}{P}{}^{r}_{k}\right)$$

$$(16d)\quad A^{i}_{jk} = \underset{1}{\nabla}_k\left(\alpha^{i}_{(2)j}\right) - 12\,D\left(\underset{1}{\nabla}_k \gamma^{i}_{j}\right) - 12\,\gamma^{l}_{j}\underset{1}{\nabla}_k \gamma^{i}_{l}.$$

$$(17)\quad \left[\underset{0}{\nabla}_k (Du^i) - D\left(\underset{0}{\nabla}_k u^i\right)\right]$$
$$= -\underset{3}{\nabla}_r u^i\left[D^2\underset{2}{P}{}^{r}_{k} - D\underset{1}{P}{}^{r}_{k} + \underset{0}{P}{}^{r}_{k}\right] + \underset{2}{\nabla}_r u^i\left[2D\underset{2}{P}{}^{r}_{k} - \underset{1}{P}{}^{r}_{k}\right]$$
$$- \underset{1}{\nabla}_r u^i\left[\underset{2}{P}{}^{r}_{k}\right] - \tfrac{1}{6}u^r\left[\underset{1}{\nabla}_k \underset{2}{P}{}^{i}_{r} - A^{i}_{rk}\right]$$

$$(18)\quad \left[\frac{\partial}{\partial t}(Du^i) - D\left(\frac{\partial u^i}{\partial t}\right)\right] = u^r\left[\frac{\partial \gamma^{i}_{r}}{\partial t}\right] - \underset{3}{\nabla}_r u^i\left[\frac{\partial \alpha^{r}}{\partial t}\right]$$

$$(19)\quad \left[\underset{2}{\nabla}_k\left(\frac{\partial u^i}{\partial t}\right) - \frac{\partial}{\partial t}\left(\underset{2}{\nabla}_k u^i\right)\right] = 3\underset{3}{\nabla}_r u^i\left[\frac{\partial \gamma^{r}_{k}}{\partial t}\right]$$

$$(20)\quad \left[\underset{1}{\nabla}_k\left(\frac{\partial u^i}{\partial t}\right) - \frac{\partial}{\partial t}\left(\underset{1}{\nabla}_k u^i\right)\right]$$
$$= 2\underset{2}{\nabla}_r u^i\left[\frac{\partial \gamma^{r}_{k}}{\partial t}\right] + \tfrac{1}{2}\underset{3}{\nabla}_r u^i\left[\frac{\partial}{\partial t}\underset{2}{P}{}^{r}_{k} + \underset{2}{\nabla}_k\left(\frac{\partial \alpha^{r}}{\partial t}\right)\right]$$

$$(21)\quad \left[\underset{0}{\nabla}_k\left(\frac{\partial u^i}{\partial t}\right) - \frac{\partial}{\partial t}\left(\underset{0}{\nabla}_k u^i\right)\right]$$
$$= u^r\left[2\underset{2}{\nabla}_l \gamma^{i}_{r}\left(\frac{\partial \gamma^{l}_{k}}{\partial t}\right) + \tfrac{1}{2}\gamma^{i}_{r(3)l}\left(\frac{\partial}{\partial t}\underset{2}{P}{}^{l}_{k} + \underset{2}{\nabla}_k \frac{\partial \alpha^{l}}{\partial t}\right) - \underset{1}{\nabla}_k\left(\frac{\partial \gamma^{i}_{r}}{\partial t}\right)\right]$$
$$+ \underset{1}{\nabla}_r u^i\left[\frac{\partial \gamma^{r}_{k}}{\partial t}\right] + \tfrac{1}{6}\underset{2}{\nabla}_r u^i\left[5\frac{\partial}{\partial t}\underset{2}{P}{}^{r}_{k} + \underset{2}{\nabla}_k \frac{\partial \alpha^{r}}{\partial t}\right]$$
$$+ \underset{3}{\nabla}_r u^i\left[\underset{1}{\nabla}_k \frac{\partial \alpha^{r}}{\partial t} + \tfrac{1}{2}\frac{\partial \alpha^{l}}{\partial t}\left(\underset{2}{P}{}^{r}_{k(3)l} + 4\underset{2}{\nabla}_k \gamma^{r}_{l}\right)\right.$$
$$\left. - \tfrac{1}{2}D\left(\frac{\partial}{\partial t}\underset{2}{P}{}^{r}_{k} + \underset{2}{\nabla}_k \frac{\partial \alpha^{r}}{\partial t}\right)\right].$$

Thus we find the following to be tensors :

$$\underset{2}{P}{}^{i}_{r},\ \underset{1}{P}{}^{i}_{r},\ \underset{0}{P}{}^{i}_{r},\ \gamma^{i}_{j(3)k},\ \underset{2}{\nabla}_k \gamma^{i}_{j},\ \underset{3}{\nabla}_k \underset{1}{\nabla}_j \gamma^{i}_{r},\ \underset{2}{\nabla}_k \underset{1}{\nabla}_j \gamma^{i}_{r},\ \underset{1}{\nabla}_k \underset{1}{\nabla}_j \gamma^{i}_{r},\ A^{i}_{jk},\ \epsilon^{i} \text{ and } \frac{\partial \alpha^{i}}{\partial t}.$$

But some of these are expressible in terms of the simpler ones, as is seen below :

$$(22)\quad \underset{2}{\nabla}_k \gamma^{i}_{j} = -\tfrac{3}{10}\underset{2}{P}{}^{i}_{j(3)k} - \tfrac{1}{5}\underset{2}{P}{}^{i}_{k(3)j} - 3\,D\gamma^{i}_{j(3)k}$$

$$(23)\quad \underset{3}{\nabla}_k \underset{1}{\nabla}_j \gamma^{i}_{r} = \underset{1}{\nabla}_j\left(\gamma^{i}_{r(3)k}\right) - 2\left(\underset{2}{\nabla}_l \gamma^{i}_{r}\right)\left(\gamma^{l}_{j(3)k}\right)$$
$$- \tfrac{1}{2}\gamma^{i}_{r(3)l}\left(\underset{2}{P}{}^{l}_{j(3)k} + 4\underset{2}{\nabla}_j \gamma^{l}_{k}\right)$$

$$(24)\quad \underset{2}{\nabla}_k \underset{1}{\nabla}_j \gamma^{i}_{r} = \underset{1}{\nabla}_j\left(\underset{2}{\nabla}_k \gamma^{i}_{r}\right) - 2\left(\underset{2}{\nabla}_l \gamma^{i}_{r}\right)\left(\underset{2}{\nabla}_k \gamma^{l}_{j}\right)$$
$$- \tfrac{1}{2}\gamma^{i}_{r(3)l}\left(\underset{2}{\nabla}_k \underset{2}{P}{}^{l}_{j} + \underset{2}{\nabla}_j \underset{2}{P}{}^{l}_{k} + 6D\underset{2}{\nabla}_j \gamma^{l}_{k}\right)$$

$$(25)\quad \mathrm{A}^i_{jk} = \tfrac{3}{5}\,(2\underset{2}{\nabla}_k \underset{1}{\mathrm{P}}{}^i_j + 3\underset{2}{\nabla}_j \underset{1}{\mathrm{P}}{}^i_k) - \tfrac{2}{5}\,(2\underset{1}{\nabla}_k \underset{2}{\mathrm{P}}{}^i_j + 3\underset{1}{\nabla}_j \underset{2}{\mathrm{P}}{}^i_k)$$
$$+ \tfrac{12}{5}\,\mathrm{D}^2\,(2\underset{2}{\nabla}_k \gamma^i_j + 3\underset{2}{\nabla}_j \gamma^i_k) + \tfrac{6}{5}\,\underset{2}{\mathrm{P}}{}^i_r\,(2\underset{2}{\nabla}_k \gamma^r_j + 3\underset{2}{\nabla}_j \gamma^r_k)$$
$$- \tfrac{24}{5}\,(\underset{2}{\nabla}_k \gamma^i_r)\,\underset{2}{\mathrm{P}}{}^r_j - \tfrac{36}{5}\,(\underset{2}{\nabla}_j \gamma^i_r)\,\underset{2}{\mathrm{P}}{}^r_k + \tfrac{36}{5}\,\mathrm{D}\underset{22}{\mathrm{R}}{}^i_{jk} - \tfrac{36}{5}\,\mathrm{D}^2\underset{32}{\mathrm{R}}{}^i_{jk}.$$

From the above formulæ it follows that the following is a complete set of intrinsic invariants for the space under consideration.

$$(26)\quad x^{(1)i},\ \underset{\gamma}{\mathrm{P}}{}^i_j\ (\gamma = 0, 1, 2),\ \gamma^i_{j(3)k},\ \underset{1}{\nabla}_k \underset{1}{\nabla}_j \gamma^i_r \text{ and } \frac{\partial \alpha^i}{\partial t}.$$

The following relationships hold among these invariants.

$$(27)\quad \text{(i)}\quad \underset{1}{\nabla}_k (x^{(1)i}) = \delta^i_k$$

$$\text{(ii)}\quad \underset{0}{\nabla}_k x^{(1)i} = x^{(1)r}\,[\underset{22}{\mathrm{R}}{}^i_{kr} - \mathrm{D}\underset{32}{\mathrm{R}}{}^i_{kr} - \gamma^i_{k(3)l}\,\underset{2}{\mathrm{P}}{}^l_r]$$
$$- 2\,(\underset{2}{\nabla}_r \gamma^i_k)\,(\mathrm{D}x^{(1)r}) - 3\gamma^i_{k(3)r}\,(\mathrm{D}^2x^{(1)r}) - \epsilon^i_{(3)k}.$$

$$\text{(iii)}\quad \underset{1}{\nabla}_k \underset{0}{\nabla}_j x^{(1)i} = \underset{22}{\mathrm{R}}{}^i_{jk} - \mathrm{D}\underset{32}{\mathrm{R}}{}^i_{jk} + (\underset{1}{\nabla}_k \underset{1}{\nabla}_j \gamma^i_r)\,x^{(1)r}$$

$$\text{(iv)}\quad \underset{2}{\nabla}_k \underset{0}{\nabla}_j x^{(1)} = -(\underset{2}{\nabla}_k \gamma^i_j) + (\underset{2}{\nabla}_k \underset{1}{\nabla}_j \gamma^i_r)\,x^{(1)r}$$

$$\text{(v)}\quad \underset{3}{\nabla}_k \underset{0}{\nabla}_j x^{(1)i} = -\gamma^i_{j(3)k} + (\underset{3}{\nabla}_k \underset{1}{\nabla}_j \gamma^i_r)\,x^{(1)r}$$

$$\text{(vi)}\quad \mathrm{D}^3x^{(1)i} = -\epsilon^i - \tfrac{1}{4}\,\underset{1}{\mathrm{P}}{}^i_r\,x^{(1)r} - \tfrac{1}{2}\,\underset{2}{\mathrm{P}}{}^i_r\,(\mathrm{D}x^{(1)r})$$

$$\text{(vii)}\quad \mathrm{D}\epsilon^i = (\underset{0}{\mathrm{P}}{}^i_r - \tfrac{1}{4}\mathrm{D}\underset{1}{\mathrm{P}}{}^i_r)\,x^{(1)r} + (\tfrac{3}{4}\underset{1}{\mathrm{P}}{}^i_r - \tfrac{1}{2}\mathrm{D}\underset{2}{\mathrm{P}}{}^i_r)\mathrm{D}x^{(1)r} + \tfrac{1}{2}\underset{2}{\mathrm{P}}{}^i_r(\mathrm{D}^2x^{(1)r})$$

$$\text{(viii)}\quad \underset{2}{\nabla}_k \epsilon^i = \tfrac{1}{2}\underset{2}{\mathrm{P}}{}^i_k - x^{(1)r}\,[\tfrac{1}{4}\mathrm{A}^i_{kr} + (\underset{2}{\nabla}_k \gamma^i_l)\,\underset{2}{\mathrm{P}}{}^l_r + 3\mathrm{D}\underset{22}{\mathrm{R}}{}^i_{rk} - 3\mathrm{D}^2\underset{32}{\mathrm{R}}{}^i_{rk}]$$
$$- \tfrac{1}{2}\mathrm{D}x^{(1)r}\,[\underset{2}{\nabla}_k \underset{2}{\mathrm{P}}{}^i_r + 6\mathrm{D}\underset{2}{\nabla}_k \gamma^i_r]$$
$$- 3(\underset{2}{\nabla}_k \gamma^i_r)\,(\mathrm{D}^2x^{(1)r}) - 3\mathrm{D}\,(\underset{0}{\nabla}_k x^{(1)i}).$$

$$\text{(ix)}\quad \underset{1}{\nabla}_k \epsilon^i = \tfrac{3}{4}\underset{1}{\mathrm{P}}{}^i_k - x^{(1)r}\,[\tfrac{1}{4}\,\underset{1}{\nabla}_k \underset{1}{\mathrm{P}}{}^i_r + \underset{2}{\nabla}_l \gamma^i_r\,(2\mathrm{D}\underset{2}{\mathrm{P}}{}^l_k - \underset{1}{\mathrm{P}}{}^l_k)$$
$$- \gamma^i_{r(3)l}\,(\mathrm{D}^2\underset{2}{\mathrm{P}}{}^l_k - \mathrm{D}\underset{1}{\mathrm{P}}{}^l_k + \underset{0}{\mathrm{P}}{}^l_k)$$
$$+ \tfrac{1}{3}\,\mathrm{D}\mathrm{A}^i_{rk} - \tfrac{1}{3}\,\mathrm{D}\,\underset{1}{\nabla}_k \underset{2}{\mathrm{P}}{}^i_r]$$
$$- \tfrac{1}{2}\mathrm{A}^i_{rk}\,(\mathrm{D}x^{(1)r}) - 3\,\mathrm{D}^2\,(\underset{0}{\nabla}_k x^{(1)i}) - \tfrac{1}{2}\,\underset{2}{\mathrm{P}}{}^i_r\,(\underset{0}{\nabla}_k x^{(1)r})$$
$$+ \underset{2}{\mathrm{P}}{}^r_k\,(\underset{0}{\nabla}_r x^{(1)i}).$$

$$(x)\quad \underset{0}{\nabla}_k \epsilon^i = \underset{0}{P}{}^i_k - \tfrac{1}{2}\underset{2}{P}{}^i_r \underset{2}{P}{}^r_k - (\underset{0}{\nabla}_r x^{(1)i})\,(D\underset{2}{P}{}^r_k - \underset{1}{P}{}^r_k) - D^3(\underset{0}{\nabla}_k x^{(1)i})$$
$$- \tfrac{1}{4}\underset{1}{P}{}^i_r(\underset{0}{\nabla}_k x^{(1)r}) - \tfrac{1}{2}\underset{2}{P}{}^i_r D(\underset{0}{\nabla}_k x^{(1)r}) + 3\underset{2}{P}{}^r_k D(\underset{0}{\nabla}_r x^{(1)i})$$
$$- x^{(1)r}\Big[\tfrac{1}{4}\underset{0}{\nabla}_k \underset{1}{P}{}^i_r + 2(D\underset{2}{\nabla}_l \gamma^i_r)(2D\underset{2}{P}{}^l_k - \underset{1}{P}{}^l_k)$$
$$+ \underset{2}{\nabla}_l \gamma^i_r (D^2\underset{2}{P}{}^l_k - \underset{0}{P}{}^l_k) - \gamma^i_{r(3)l}(D^3\underset{2}{P}{}^l_k - D^2\underset{1}{P}{}^l_k + D\underset{0}{P}{}^l_k)$$
$$- 2(D\gamma^i_{r(3)l})(D^2\underset{2}{P}{}^l_k - D\underset{1}{P}{}^l_k + \underset{0}{P}{}^l_k)$$
$$+ \tfrac{1}{12}\underset{2}{P}{}^i_l(A^l_{rk} - \underset{1}{\nabla}_k \underset{2}{P}{}^l_r) + \tfrac{1}{6}D^2(A^i_{rk} - \underset{1}{\nabla}_k \underset{2}{P}{}^i_r)$$
$$- \tfrac{1}{6}\underset{2}{P}{}^l_k(A^i_{rl} - \underset{1}{\nabla}_l \underset{2}{P}{}^i_r)\Big]$$
$$- Dx^{(1)r}\Big[\tfrac{1}{2}\underset{0}{\nabla}_k \underset{2}{P}{}^i_r + 3\underset{2}{\nabla}_l \gamma^i_r(2D\underset{2}{P}{}^l_k - \underset{1}{P}{}^l_k) + \tfrac{1}{2}DA^i_{rk}$$
$$- 3\gamma^i_{r(3)l}(D^2\underset{2}{P}{}^l_k - D^2\underset{1}{P}{}^l_k + \underset{0}{P}{}^l_k) - \tfrac{1}{2}D\underset{1}{\nabla}_k \underset{2}{P}{}^i_r\Big]$$
$$- \tfrac{1}{2}(D^2x^{(1)r})[A^i_{rk} - \underset{1}{\nabla}_k \underset{2}{P}{}^i_r].$$

$$(xi)\quad \frac{\partial\epsilon^i}{\partial t} = \frac{\partial\alpha^i}{\partial t} - x^{(1)r}\Big[\tfrac{1}{4}\underset{1}{\nabla}_r \frac{\partial\alpha^i}{\partial t} + \frac{\partial\gamma^i_l}{\partial t}\underset{2}{P}{}^l_r\Big]$$
$$- \tfrac{1}{2}Dx^{(1)r}\Big[\underset{2}{\nabla}_r \frac{\partial\alpha^i}{\partial t}\Big] - 3\frac{\partial\gamma^i_r}{\partial t}(D^2x^{(1)r}).$$

Remarks.

In a previous note† I have included A^i_{jk} in the list of fundamental invariants for path spaces of order 2. On later calculation it has been found that A^i_{jk} is not a fundamental tensor, but can be derived from $\gamma^i_{j(2)k}$ and the curvature tensors. In fact

$$A^i_{jk} = \tfrac{3}{2}\underset{2}{\nabla}_k \underset{0}{P}{}^i_j + \tfrac{3}{2}D\underset{2}{\nabla}_k \underset{1}{P}{}^i_j + \tfrac{3}{2}\underset{1}{\nabla}_j \underset{1}{P}{}^i_k - \tfrac{1}{2}\underset{1}{\nabla}_k \underset{1}{P}{}^i_j$$
$$+ 6D^2\gamma^i_{j(2)k} + \tfrac{3}{2}\underset{1}{P}{}^i_r \gamma^r_{j(2)k} - \tfrac{9}{2}\gamma^i_{r(2)k}\underset{1}{P}{}^r_j.$$

Hence the list of fundamental intrinsic invariants for the space consists *only* of

$$x^{(1)i},\ \underset{1}{P}{}^i_j,\ \underset{0}{P}{}^i_j,\ \gamma^i_{j(2)k},\ \underset{1}{\nabla}_k \underset{1}{\nabla}_j \gamma^i_r \text{ and } \frac{\partial\alpha^i}{\partial t}.$$

From this and the formula (26) of this paper, we are led to expect that the fundamental intrinsic invariants for path spaces of order σ will consist only of

$$x^{(1)i},\ \underset{\gamma}{P}{}^i_j\ (\gamma = 0, 1, \cdots \sigma - 1),\ \gamma^i_{j(\sigma)k},\ \underset{1}{\nabla}_k \underset{1}{\nabla}_j \gamma^i_r \text{ and } \frac{\partial\alpha^i}{\partial t}.$$

† *Loc. cit.*, p. 164, formula (22).

I am thankful to Prof. Kosambi for drawing my attention to this.

THE PARAMAGNETIC SUSCEPTIBILITY OF LITHIUM.

By S. Ramachandra Rao and S. Sriraman.

(From the Annamalai University, Annamalainagar.)

Received March 30, 1937.

1. *Introduction.*

The subject of the susceptibility of the alkali metals has assumed great interest in recent years because of the theoretical importance attaching to such measurements from the point of view of the weak spin paramagnetism of the conduction electrons in metals. Pauli's[1] theory modified by Landau[2] leads to the following expression for the susceptibility of the conduction electrons.

$$(\chi_A)_e \times 10^6 = 32 \cdot 11 \frac{q}{V_0} \qquad (1)$$

where $(\chi_A)_e$ is the gram atomic susceptibility due to the electrons, q the number of free electrons per atom and V_0 the width of the energy band occupied by these electrons in volts. For prefectly free electrons, this energy band will be of the order of a few volts.[3] Landau[4] has also shown that the diamagnetic contribution by the conduction electrons is expressed by

$$\chi_L = 0 \cdot 623 \; n_0^{\frac{1}{3}} \; \rho^{-\frac{2}{3}} \; A^{-\frac{1}{3}} \times 10^{-6} \qquad (2)$$

where χ_L is the mass susceptibility, n_0 the number of free electrons per atom, ρ the density and A the atomic weight. Since free electrons give a paramagnetic effect due to electron spin, which is just three times as great as the Landau diamagnetism, the contribution of these electrons to the total susceptibility is

$$2\chi_L = 1 \cdot 246 \; n_0^{\frac{1}{3}} \; \rho^{-\frac{2}{3}} \; A^{-\frac{1}{3}} \times 10^{-6}$$

Lithium is of special interest since the contribution to the susceptibility of the metal by the ion core (Li^+) is small being $-0 \cdot 7$.[5] In this element therefore almost the entire susceptibility is due to the contribution by the conduction electron occupying the 2*s* level. A study of the susceptibility of lithium will therefore lead to much useful information regarding the paramagnetism of the free electrons.

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1 *Zeits. f. Phys.*, 1927, **41**, 81; see also Stoner, *Magnetism and Matter*, 1934, 504.

2 *Zeits. f. Phys.*, 1930, **64**, 629. See also Peierls, *Zeits. f. Phys.*, 1933, **80**, 763; 1933, **81**, 186.

3 Mott and Jones, *Properties of Metals and Alloys*, 1936, 54.

4 *Zeits. f. Phys.*, 1930, **64**, 629.

5 Hoare and Brindley, *Proc. Roy. Soc.*, 1934, **147**, 88; 1935, **152**, 342; also Angus, *Proc. Roy. Soc.*, 1932, **136**, 573.

Note.—All susceptibility values in this paper are given in 10^{-6} units.

In their classical study of the magnetic properties of elements, Honda[6] and Owen[7] included the alkali metals. Owen studied lithium and gave 0·5 as the most probable value. As a matter of fact, he investigated two Kahlbaum specimens and one sample from Merck. Of the Kahlbaum metals, one had a value of 0·50 which was independent of the field intensity and the other had values ranging from 10·06 to 3·36 when the intensity of the field was varied from 5 to 15 kilogauss. This at infinite field gave a value of 0·25. The Merck specimen had susceptibilities varying from 5·1 to 3·8 in the range 10 to 25 kilogauss, leading to a value of 3·11 at infinite field strength.

Although the susceptibilities of Na, K, Rb and Cs have been reinvestigated by Sucksmith,[8] McLennan, Ruedy and Cohen[9] and Lane,[10] no study has been made of lithium. It appeared therefore to be of interest to repeat the measurements of Owen on lithium.

2. *Experiment.*

The substance was available in the form of cubes from Kahlbaum. It was necessary to take small quantities in glass bulbs for investigation by the Curie method. A tube as shown in Fig. 1 was used for this purpose. Pyrex

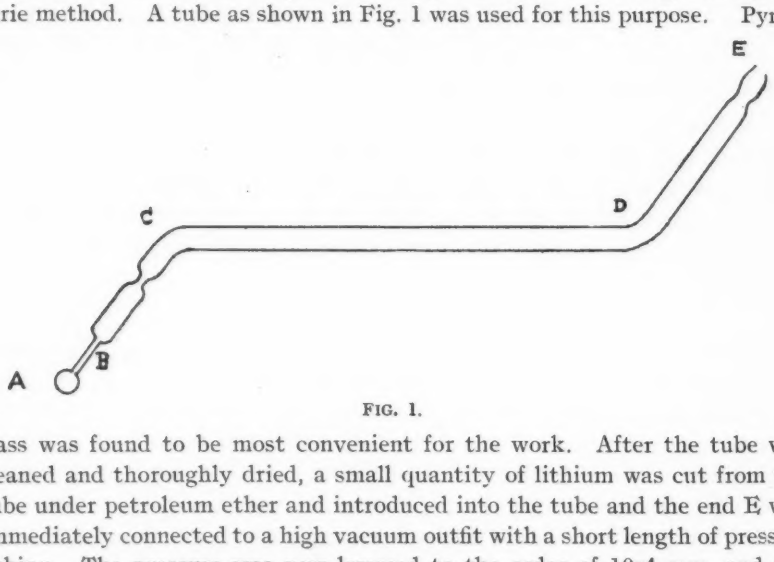

FIG. 1.

glass was found to be most convenient for the work. After the tube was cleaned and thoroughly dried, a small quantity of lithium was cut from the cube under petroleum ether and introduced into the tube and the end E was immediately connected to a high vacuum outfit with a short length of pressure tubing. The pressure was now lowered to the order of 10^{-4} mm. and the

[6] *Ann. der Phys.*, 1910, **32**, 1027.
[7] *Ann. der Phys.*, 1912, **37**, 657.
[8] *Phil. Mag.*, 1926, **2**, 21.
[9] *Proc. Roy. Soc.*, 1927, **116**, 468.
[10] *Phys. Rev.*, 1930, **35**, 977.

entire length of the tube from A to C was arranged to lie just over a wire-gauze heated from below by a burner. The mean temperature to which the tube containing the metal was raised was estimated with a thermometer to be between 200° and 250°C. The metal and the inner surface of the tube were thus slowly degassed and when the pressure as measured on the McLeod gauge showed a steady reading, the molten metal was allowed to flow in the bulb A. Any adhering oxide would be removed at the constriction near C. The bulb was sealed off at B. It was a difficult process to settle exactly the temperature conditions of the tube for successful collection of lithium. If the tube was too hot, the molten lithium used to stick to the glass; a dark patch was immediately formed and the tube cracked at the place resulting in the burning of lithium. If the tube was cold, the silvery white metal would spread as a thin film which could not be successfully handled as further heating gave the effect mentioned above. When once the proper temperature conditions were grasped, it was easy to prepare several bulbs containing lithium for investigation.

The magnetic susceptibility was determined by the Curie method. The pyrex bulbs were found to be diamagnetic while lithium was paramagnetic. Hence the deflections obtained were positive (corresponding to a paramagnetic effect) or negative (corresponding to a diamagnetic effect) in accordance with the relative masses of the bulb and the metal in each case.

After determining the deflections due to the bulbs containing the metal and weighing them, the bulbs were broken open and the metal dissolved in water to which a few drops of concentrated hydrochloric acid were added. The bulbs were next cleaned with boiling distilled water and finally dried in a vacuum desiccator. The deflections due to the bulbs alone were next determined. By weighing the empty bulbs, the mass of lithium taken in each case could be determined.

It was necessary to determine the susceptibility of lithium at different field strengths to correct for the presence of ferromagnetic impurities. According to Honda,[6]

$$\chi_i = \chi_p + \frac{\sigma m}{H}$$

where χ_i and χ_p are the specific susceptibilities of the impure and pure metals, σ is the specific intensity of magnetisation of the ferromagnetic impurity, m is the mass of impurity in unit mass of the substance and H is the magnetic field intensity. If χ_i is known at different values of H, a graph could be drawn between these quantities and by extrapolating the susceptibility could be determined for $H = \infty$ or $\frac{1}{H} = 0$, when $\chi_i = \chi_p$.

This correction was essential because the metal contained appreciable ferromagnetic impurity and also since it had to be cut in small pieces with a sharp blade.

The magnetic field intensities at different currents in the electromagnet were determined with a search coil and a ballistic galvanometer which was calibrated with a solenoid.

3. *Results.*

Measurements made with eight bulbs are tabulated below.

TABLE I.

Bulb No.	Mass of lithium	Current in amps.	Deflection due to bulb and metal in cm.	Deflection due to the bulb alone in cm.	Deflection due to metal alone in cm.	χ
1	0·0218	3	+13·77	− 7·28	+21·05	5·32
		4	+19·74	−11·19	+30·93	5·00
		5	+23·03	−13·98	+37·01	4·79
		6	+24·39	−16·60	+40·99	4·39
2	0·0132	3	+ 4·20	− 5·83	+10·03	4·19
		4	+ 5·66	− 9·00	+14·66	3·92
		5	+ 6·65	−11·27	+17·92	3·83
		6	+ 7·46	−13·24	+20·70	3·66
3	0·0055	3	− 2·07	− 7·39	+ 5·32	5·12
		4	− 3·74	−11·52	+ 7·78	4·80
		5	− 4·73	−14·38	+ 9·65	4·77
		6	− 5·95	−16·79	+10·84	4·35
4	0·0074	3	− 0·45	− 4·74	+ 4·29	3·07
		4	− 0·69	− 7·27	+ 6·58	3·02
		5	− 0·98	− 9·01	+ 8·03	2·95
		6	− 1·27	−10·62	+ 9·35	2·84
5	0·0158	3	+ 4·19	− 8·42	+12·61	4·23
		4	+ 5·44	−12·90	+18·34	3·94
		5	+ 6·43	−15·98	+22·41	3·85
		6	+ 6·92	−18·88	+25·80	3·67
6	0·0146	3	+ 3·03	−10·07	+13·10	4·75
		4	+ 2·80	−15·44	+18·24	4·24
		5	+ 2·45	−19·12	+21·57	4·01
		6	+ 2·02	−22·59	+24·61	3·79
7	0·0160	3	− 1·50	−10·92	+ 9·42	3·12
		4	− 3·16	−16·74	+13·58	2·88
		5	− 4·04	−20·74	+16·70	2·84
		6	− 4·77	−24·52	+19·75	2·77
8	0·0113	3	− 2·88	−12·19	+ 9·31	4·37
		4	− 5·24	−18·67	+13·43	4·03
		5	− 7·05	−23·13	+16·08	3·87
		6	− 8·67	−27·33	+18·66	3·71

Table II gives the values of H and $\frac{1}{H}$ at different field currents.

TABLE II.

Current in amperes	H in kilogauss	$\frac{1}{H}$
3	4·32	0·232
4	5·41	0·185
5	6·21	0·161
6	6·80	0·147
7	7·10	0·141

Fig. 2 shows the graph between the susceptiblity and $\frac{1}{H}$. Plots are made for the eight specimens studied. On producing the straight line graphs in all these cases, it will be noted that they all pass through the same point on the Y-axis. This point corresponds to a value of 2·6 for the paramagnetic susceptibility of lithium. It appears therefore that Owen's estimate of 0·5

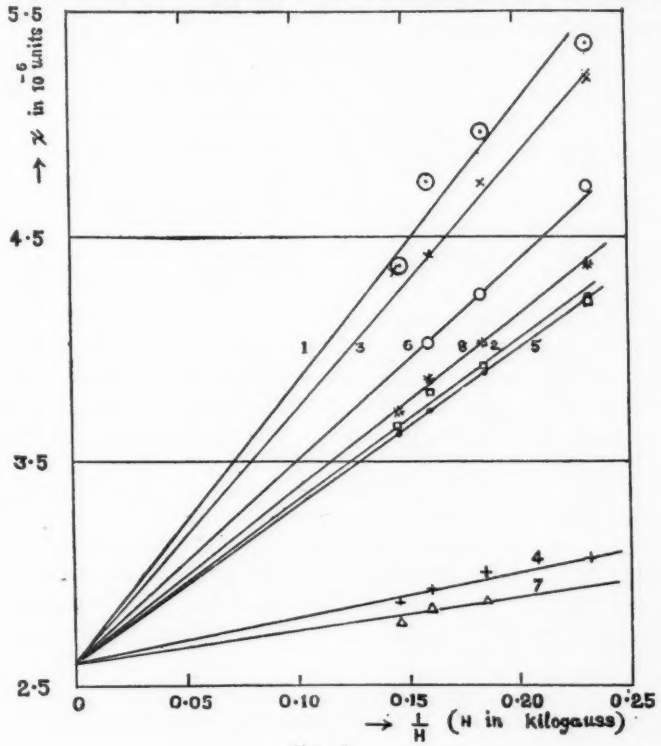

FIG. 2.

is too low and that the correct susceptibility must be much higher. It will be shown presently that some theoretical support may also be adduced to justify the higher value. Since the atomic weight of lithium is 6·94, the atomic susceptibility of lithium has the value 18·0.

4. *Discussion.*

It has been shown by theory and experiment that the ionic suspcetibility of Li^+ is $-0·7$.[5] The paramagnetic susceptibility of the free electrons in a gram atom of lithium is hence 18·7. From equation (1) we can deduce a value for V_0 the width of the energy band in volts for the free electrons. The number (q) of these electrons per atom of lithium is 1.
Hence

$$V_0 = \frac{32·11}{(\chi_A)_e} = \frac{32·11}{18·7} = 1·72 \text{ volts.}$$

O'Bryan and Skinner[11] studied the X-ray emission band of lithium and found the breadth of the band to be $4·2 \pm 0·6$ volts agreeing with Seitz's[12] calculated value of 3·5 volts. Our results indicate a narrowing of the energy band. In this respect, lithium resembles the other alkali metals. In the following table are given the values of the band width of free electrons in the alkali elements calculated in the above manner. The measurements of Lane[10] are taken for the susceptibilities (except for lithium) and the ionic values are those calculated from Flordal and Frivold's measurements[13] in the cases of Na^+ and K^+. For Rb^+ and Cs^+, the values of Kido[14] are assumed.

TABLE III.

Element.	χ_A	$(\chi_A)_{ion}$	$(\chi_A)_e$	V_0	Calculated energy band width in volts[15]
Li ..	18·0	− 0·7	18·7	1 72	3·5
Na ..	15·0	− 6·9	21·9	1 47	3·16
K ..	21·1	− 15·0	36·1	0 89	2·06
Rb ..	17·9	− 27·2	45·1	0·71	1·79
Cs ..	29·2	− 35·1	64·3	0·50	1·53

χ_A = the atomic susceptibility ;
$(\chi_A)_{ion}$ = the susceptibility of the ion per gram atom ;
$(\chi_A)_e$ = the susceptibility of the free electron per gram atom.

[11] *Phys. Rev.*, 1934, **45**, 370.
[12] *Phys. Rev.*, 1935, **47**, 400.
[13] *Ann. der Physik*, 1935, **23**, 425.
[14] *Sci. Rep. Tohoku Imp. Univ.*, 1933, **22**, 835.
[15] Values taken from Ref. 3 except for lithium for which the corrected value of Seitz (Ref. 12) is given.

There is one other direction in which theoretical deductions could be tested. As was mentioned in the introduction, the Landau diamagnetism of free electrons is given by

$$\chi_L = 0{\cdot}623\ n_0^{\frac{1}{3}}\ \rho^{-\frac{2}{3}} A^{-\frac{1}{3}} \times 10^{-6}$$

The total contribution to the paramagnetism of the metal by the free electrons is hence $2\chi_L$. Following Mott and Jones,[16] a table is given below giving the mass susceptibilities calculated from the above relations.

TABLE IV.

Elements		Li	Na	K	Rb	Cs
Density		0·534	0·97	0·86	1·52	1·87
$2\chi_L$		1·0	0·45	0·40	0·21	0·16
Diamagnetism of ions		−0·10	−0·30	−0·38	−0·32	−0·31
Total susceptibility calculated ..		0·9	0·15	0·02	−0·11	−0·15
Observed susceptibility	Honda[6] & Owen[7] ..	0·5	0·51	0·40	0·07	−0·10
	Sucksmith[8]	..	0·59	0·51	0·07	−0·05
	McLennan, Ruedy & Cohen[9] ..	..	0·59	0·45	0·17	+0·20
	Lane[10] ..	..	0·65	0·54	0·21	+0·22
	Authors ..	2·6				

An examination of the above table shows that the same discrepancy between observed and calculated values holds good as much for lithium as for the other alkali elements. Mott and Jones suggest that a narrowing of the band width (as was mentioned earlier) for the free electrons is not likely to happen in the alkali metals and that the observed discrepancy should be due to interchange forces.

5. *Summary.*

The paramagnetic susceptibility of lithium was determined by the Curie method taking small quantities of the metal in pyrex glass bulbs. The glass walls and the metal were well degassed before the metal was sealed in

[16] Mott and Jones, *Properties of Metals and Alloys*, 1936, 188.

the bulbs. The susceptibilities were determined at different field strengths and in each case the susceptibility at infinite field strength was deduced by extrapolation. The mean paramagnetic susceptibility is found to be $2{\cdot}6 \times 10^{-6}$. This value is examined in the light of theoretical calculations of the paramagnetism of free electrons and it is shown to be in harmony with the general scheme of the alkali elements.

A NEW SEPARATION OF THE COMPONENTS OF *PSORALEA CORYLIFOLIA*, LINN.

By T. R. Seshadri
and
C. Venkatarao.
(*From the Department of Chemical Technology, Andhra University, Waltair.*)

Received March 22, 1937.

These seeds (more correctly fruits) have been greatly valued for their pleasant aroma as will be evident from the Sanskrit name *sugandha* and have been widely used in medicine. Internally they are said to be useful as laxative, diuretic and anthelmintic and externally as cure for leucoderma and leprosy. They are frequently employed in several toilet preparations. Regarding chemical work on this material done in the past reference should be made to Dymock,[1] Menon,[2] Chopra and Chatterjee,[3] Chopra[4] and Jois, Manjunath and Venkatarao.[5] A sample of the seeds was sent from Trichinopoly to one of us (T. R. S.) when he was working in the Agricultural Research Institute, Coimbatore, in 1932 with a view to explore possibilities of industrial utilisation. The chemical investigation that was then begun could not be continued. Early in 1933 the paper of Jois, Manjunath and Venkatarao appeared embodying the results of a detailed chemical study. Besides examining the fixed oil of the seeds they were able to isolate two crystalline solids psoralen and isopsoralen. The latter has been identified as angelicin (Jois and Manjunath[6]) and the former has been successfully synthesised recently by Spath, Manjunath, Jois and Pailer.[7] Since however our method of study is different from those of others and it enables the components to be separated more effectively in greater purity and yield and at the same time gives information regarding the parts of the seeds in which they occur, it has been thought desirable to record our results.

A simple inspection of the seed (fruit) showed that it consisted of a sticky, oily pericarp which seemed to contain all the odour, a hard seed coat and a kernel which had no smell, contained a fixed oil and a bitter substance. It was found that it was rather difficult to powder the whole seed owing to the sticky pericarp. A few exploratory experiments indicated that almost all the pericarp could be dissolved in ether by cold percolation leaving the seed coat and kernel in tact. The ether extract contained a steam volatile essential oil, a caustic alkali soluble resin and a terpenoid liquid insoluble in

caustic alkali. From the ether-extracted material, the remaining portion of the pericarp (skin) could be easily rubbed off and the substance powdered. On extracting this powder in a Soxlet apparatus using light petroleum (sp. gr. 0·64 to 0·66) all the fixed oil was removed and along with this a colourless crystalline solid was deposited in the receiver. The essential oil, the resin and the terpenoid oil were present in the pericarp only and not in the kernel. The crystalline solid obtained during the extraction with petroi was a mixture of psoralen and isopsoralen and the fixed oil finally obtained was pale brown and devoid of any prominent odour. It was reasonably pure consisting almost completely of glycerides. A small unsaponifiable portion of the fixed oil was found to contain a sterol which appeared to be phytosterol. These were therefore components of the kernel. Besides these it contained nitrogenous and mineral matter.

All previous workers ground up the whole seed and extracted the powdered material and hence did not get pure fractions and the examination of the products was difficult. Amongst the advantages of the present method may be mentioned (1) the possibility of obtaining the components of the pericarp in three fractions, (2) a purer fixed oil free from much colour and uncontaminated with resin and (3) a better yield of the psoralen mixture which is the cause of the bitter taste of the seed. These fractions can be used conveniently to satisfy different requirements as for example where the perfume and resin are wanted the pericarp fractions could be used. A note on the physiological properties of the fractions is given towards the end of this paper.

Experimental.

Components of the pericarp. Aromatic principles and resin.—The material available in the local market was employed. The entire seed was kept soaked in ordinary ether for 12 hours, the ether extract decanted and the process repeated once again. The extraction was then practically complete and all but a thin skin was removed. In a test experiment it was found that this extraction removed about 11·7 per cent. of the whole seed. It was also noted that the whole extract was soluble in alcohol and that a portion of it was soluble in aqueous sodium hydroxide. The ether solution was therefore extracted repeatedly with 5 per cent. aqueous sodium hydroxide solution till no more was removed. The brown alkaline solution was once extracted with pure ether and then acidified with hydrochloric acid. A dark brown semi-solid resin separated (8·6 per cent. by weight of the seed). It did not possess any definite smell or taste. It slowly solidified to a brittle solid on keeping. The ether solution

containing the alkali insoluble matter was distilled to remove the solvent. The residue was a viscous brown-red oil possessing all the odour of the seed (3·1 per cent.). On passing steam through it an almost colourless essential oil came over (0·05 per cent.). It was obtained from the distillate by ether extraction. It smelt strongly of the seed and had the refractive index 1·4808 at 30°C. The fraction in the distilling flask had still some odour of the seed. For purposes of further examination it was taken up in ether, dried over calcium chloride and the ether removed. The residual brown viscous oil when distilled under reduced pressure underwent decomposition to a thicker oil. Some of its properties were as below :

Specific gravity	0·9759
Refractive index	1·5310
Saponification value ..	21·0
Unsaponifiable matter ..	87·5
Iodine value	92·2

It was completely soluble in petroleum ether and seemed to consist mostly of complex terpenoid compounds. The pericarp gave tests for the presence of a pigment of the nature of hydroxy flavone giving yellow colour with alkali. But since the quantity present was very small it was not further investigated.

Components of the Kernel. Psoralen-Isopsoralen mixture and the fixed oil.—The ether-extracted seed was cleaned by rubbing, powdered and extracted with light petroleum (sp. gr. 0·64 to 0·66) in a Soxlet apparatus for about 12 hours. Vigorous extraction for this period effected complete extraction. After about three hours, a crystalline deposit was invariably noticed in the receiver and this increased in bulk as the extraction progressed. The extract was then set aside for a few days, filtered under suction and the solid washed with small quantities of light petroleum in order to remove all the adhering oil. After drying, the solid was obtained in a yield of 1·1 per cent. of the crushed seed or 0·97 per cent. of the fresh seed (Jois, Manjunath and Venkatarao, 0·27 per cent.). It was bitter to the taste, was moderately soluble in boiling water, easily in alcohol or chloroform and sparingly in ether and petroleum ether. It melted at about 110–115° C. and it could be separated into psoralen (m.p. 168–69°C.) and isopsoralen (m.p. 141–42°C.) by fractional crystallisation as already outlined by Jois, Manjunath and Venkatarao. The former is the less soluble of the two and always comes down as large hard crystals whereas the latter crystallises as finer and softer needles.

When the light petroleum extract was distilled on a water-bath to remove the solvent, a fixed oil was obtained with a pale brown colour. The solvent was completely removed by passing a current of nitrogen. The

yield was then 11 per cent. of the powdered seed or about 10 per cent. of the fresh seed. An attempt was made to get a colourless oil by soaking the ether-extracted seed in water, rubbing very well, drying in the sun and then powdering and extracting. But this did not effect any appreciable change. The oil was rather viscous and had still a bitter taste. With a view to estimate if any considerable amount of psoralen or isopsoralen was present in it, about 40 g. of the oil was saponified and the unsaponifiable fraction removed by ether extraction of the alkaline solution. The acids were then liberated by strongly acidifying the solution and the mixture was then warmed. During this process the bitter principles which are coumarins would have been first dissolved in the alkali undergoing hydrolysis and subsequently been reformed on acidifying and heating. Then they would be insoluble in aqueous sodium carbonate. In the collected solid the portion that was insoluble in sodium carbonate was very small showing that the whole solid was composed almost completely of fatty acids and the bitter substances were present only in very small quantities.

The fixed oil obtained was examined for some of its properties with a view to note how far it differed from the previous specimens and the physical constants are given below :

	Our sample	Sample of Jois, Manjunath and Venkatarao
Specific gravity	0·9283 at 30° C.	0·9692 at 25° C.
Refractive index	1·4739 at 30° C.	1·5132 at 25° C.
Acid value	8·01	19·9
Saponification value	194·7	117·2
Iodine value	96·4	96·9
Insoluble acids (fatty and resin acids)	90·5	69·0
Unsaponifiable matter ..	1·72	27·0

The figures clearly indicate that our sample is free from resins and terpenoid hydrocarbons which obviously contaminated the samples of previous workers. The high value for unsaponifiable matter was due to the presence of alkali-insoluble terpenoid compounds which we have separated from the pericarp. High acid value and low saponification value may be due to the presence of resins and hydrocarbons. The high percentage of insoluble acids in our sample along with other figures shows that it is almost pure glyceride. Further since our sample was not coloured there was no difficulty in the determination of the saponification and acid values.

Fatty acids.—About 10 g. of the oil was saponified with alcoholic potash, diluted with water and after removing by ether extraction the unsaponifiable fraction, acidified. The insoluble fatty acids thereby precipitated were extracted with light petroleum, dried over anhydrous calcium chloride and the solvent removed. The yield of the mixed fatty acids was 90·5 per cent. of the oil (Jois *et al*, 69 per cent.). It consisted of a mixture of some colourless crystalline solid and a faint brown liquid. The following properties of the mixture were noted :

		Jois *et al*
Iodine value	113·1	108·4
Mean molecular weight ..	302·3	378·6
Resin acids (Twitchell's volumetric method)	1·01%	21·5%

The separation of the saturated and unsaturated fatty acids by Twitchell's lead salt method did not offer any difficulty since the percentage of the resin acids was very small. In an estimation the value for the saturated acids was found to be 22·4 per cent. the rest being taken as undsaturated acids. The properties of the two fractions are given below :

	Satured		Unsatured	
	Our value	Jois *et al*	Ours	Jois *et al*
Percentage yield from oil ..	20·05	13·0	69·5	41·3
Iodine value	0·42	3·5	136·2	157·5
Mean molecular weight ..	311·5	294·5	316·0	320·0

Unsaponifiable matter. Isolation of a sterol acetate.—From the unsaponifiable matter a small quantity of a sterol was isolated. It could not be crystallised though it gave all the characteristic tests satisfactorily. It was therefore acetylated with acetic anhydride and sodium acetate (boiling for 3 hours), poured into a large volume of water and the solid crystallised from 95 per cent. alcohol. It was obtained as colourless plates melting at 126–28°C. and hence the sterol seemed to be phytosterol.

The cake.—The cake left behind after the removal of the oil was slightly bitter to the taste and this bitterness could be removed by boiling it with a little water. This taste was possibly due to a small amount of psoralen and isopsoralen. With a view to examine if there was much left, the cake was extracted twice by boiling with alcohol for 6 hours and the solvent distilled off. A very small quantity of solid was obtained thereby showing that almost all had been extracted by the petroleum.

The cake contained about 6·7 per cent. nitrogen (Kjeldahl) and about

7·75 per cent. of ash. The main components of the mineral matter were calcium, potassium, phosphates and silicates; iron, aluminium, magnesium, chloride and sulphate were present in small quantities only.

Physiological properties of the various fractions.—The utility of these for skin affections has been examined in the King George Hospital, Vizagapatam. The alkali-soluble resin had no effect and the alkali-insoluble terpenoid oil including the volatile oil had a pronounced depilatory property and no other influence. The volatile oil was not separately tried since it was very small in quantity. The fatty oil produced strong reaction on the skin particularly in cases of leucoderma and so also the bitter solids (psoralen and isopsoralen) when applied as a paste with lanolin. However, the work is still in progress and no definite statement could be made at this stage. We thank Dr. V. Iswariah for kindly undertaking this part of investigation.

Summary.

The components of the seeds have been obtained in a greater number of fractions which are fairly homogeneous by using a new method of analysis. It consists in extracting the entire seed with ether in the cold thereby removing all the components of the pericarp. This portion has been separated as the volatile essential oil, non-volatile terpenoid oil and alkali-soluble resin. The rest of the seed is crushed and extracted with petroleum ether. This gives rise to a good yield of the bitter principles as crystalline solids and the fixed oil in a pure condition. The physical and chemical properties of the pure fixed oil and its component acids and certain properties of the terpenoid oil have been studied in detail. A sterol (Phytosterol) in the form of its acetate has been isolated from the unsaponifiable portion of the fixed oil. The residual cake contains only traces of the bitter solid, a good percentage of proteins and mineral matter and is suitable as a feeding stuff and manure. Some of the fractions have definite action on the skin.

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PIGMENTS OF COTTON FLOWERS.

Part IV. Constitution of Herbacitrin and Herbacetin—New Glucoside and Aglucone (Flavonol).

By K. Neelakantam
and
T. R. Seshadri.
(*From the Department of Chemistry, Andhra University, Waltair.*)

Received February 23, 1937.

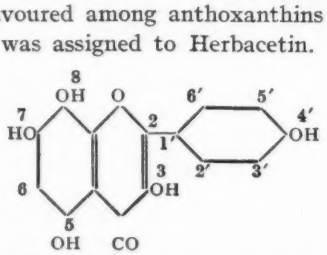
The isolation of a new flavonol glucoside from *Gossypium herbaceum* (Uppam) was recorded in a previous paper.[1] Though its constitution was known at that time the publication of our results was postponed till they could be confirmed by synthesis. It has been named Herbacitrin since it was first obtained from *Gossypium herbaceum* and since there already exists another similar substance with the name Gossypitrin. The corresponding aglucone which is a flavonol has received, therefore, the name Herbacetin. These have been found to occur in *Gossypium indicum* (Karunganni) also.[2]

Herbacitrin is a monoglucoside having the formula $C_{21}H_{20}O_{12}$ and it gives on hydrolysis with acids glucose and an aglucone (Herbacetin) of the composition $C_{15}H_{10}O_7$. Since they undergo oxidation in alkaline solution exposed to air, they belong to the flavonol series. They are isomeric with Quercimeritrin and Quercetin respectively to which they bear some resemblance particularly in their melting points and those of their derivatives, and in their colour reactions with ferric chloride and lead acetate. On closer examination, however, the differences become evident. The following table sums up these characteristics:

	Herbacitrin	Quercimeritrin
1. Melting point	247–49°	246–48°
2. Melting point of acetyl derivative ..	214–16°	216–17°
3. $FeCl_3$ colour-reaction	Olive green	Olive green
4. Lead acetate colour reaction ..	Red precipitate	Red precipitate
5. Formula of hydrate	$C_{21}H_{20}O_{12}$, $2H_2O$	$C_{21}H_{20}O_{12}$, $3H_2O$

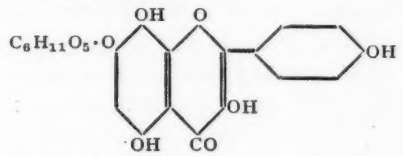
	Herbacetin	Quercetin
1. Melting point	280–83°	310–12°
2. Melting point of acetyl derivative ..	192–93°	197–98°
3. $FeCl_3$ colour reaction	Olive green	Olive green
4. Lead acetate colour reaction ..	Red precipitate	Red precipitate
5. Formula of hydrate	$C_{15}H_{10}O_7$, H_2O	$C_{15}H_{10}O_7$, $2H_2O$

The most remarkable difference between the isomeric pairs exists in their reactions towards alkaline buffer solutions of different pH values. Quercimeritrin and Quercetin give only yellow colours which fade slowly whereas Herbacitrin produces first yellow rapidly changing to emerald green just like Gossypitrin, and Herbacetin gives a bright blue after the initial yellow just like Gossypetin. In these colour reactions the resemblance between Gossypitrin and Herbacitrin, and between Gossypetin and Herbacetin is very close. They resemble also in their colour reactions with ferric chloride and lead acetate. Further a very useful observation in connection with the constitution of the new anthoxanthins is that they give the gossypetone reaction quite similar to Gossypitrin and Gossypetin. From the above reactions and the fact that Herbacitrin occurs in the cotton flowers side by side with Gossypitrin, it was deduced that the new glucoside and aglucone should have constitutions similar to Gossypitrin and Gossypetin as far as the benzopyrone portion of the molecules were concerned, that is, three of the five hydroxyl groups in Herbacetin should be in positions 5, 7 and 8. Since Herbacetin is a flavonol and the 4′-position in the hydroxy-phenyl nucleus is the most favoured among anthoxanthins and anthocyanins, the following constitution was assigned to Herbacetin.



This was confirmed by the oxidation of the glucoside by air in aqueous alkaline solution whereby *p*-hydroxy-benzoic acid was produced and isolated after methylation as anisic acid and identified.

The position of the glucose residue in Herbacitrin is tentatively fixed as 7 by analogy with Gossypitrin and Quercimeritrin (see Attree and Perkin[3]) which it resembles. Position 4′ was not considered probable in view of the fact that no instances are known among anthoxanthins in which the hydroxyphenyl nucleus carries the sugar residue, and Herbacitrin yields *p*-hydroxybenzoic acid on oxidation in alkaline solution. From the colour reaction with lead acetate and the difficulty with which it undergoes hydrolysis it could be concluded that Herbacitrin is not a 3-glucoside. Its ready oxidation to give the gossypetone reaction and its reformation with sulphurous acid show that positions 5 and 8 are free to form a *para*-quinonoid structure. The *ortho*-quinonoid structure does not seem to be so easily formed since Quercetagetin which has hydroxyl groups in the 5, 6 and 7 positions does not give the gossypetone reaction. Position 7 therefore is left as the most probable one for the glucose residue.



The yield of Herbacitrin is at best very small and it varies from sample to sample of the flower petals. Frequently its separation from the accompanying Gossypitrin and Quercetin and further purification become laborius thus reducing the yield considerably. This has to a great extent restricted the scope of our investigations on its constitution, and the best method under the circumstances of placing it on a secure basis was its synthesis. The compound 3 : 5 : 7 : 8 : 4′-pentahydroxy flavone has now been synthesised in the Dyson Perrins Laboratories in Oxford (private communication from Professor R. Robinson, F.R.S.). He has very kindly compared the synthetic flavonol and its acetyl derivative with the specimens obtained from the natural source and found them to be identical in all respects including the colours given in alkaline buffer solutions. Our thanks are therefore due to him for this kindness.

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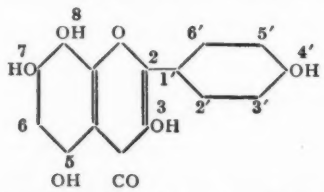
The first isolation of Herbacitrin has already been described (see Neelakantam, Seshadri and Rao[1]). In order to get more of it about 2 kg. of the dry Uppam petals kindly supplied to us by the Cotton Specialist, Coimbatore, last season (1936) were extracted with methylated spirits as usual and the extract concentrated to small bulk (800 c.c.). On allowing it to stand for several days, only a small amount of Gossypitrin (2 g.) separated out, contrary

	Herbacetin	Quercetin
1. Melting point	280–83°	310–12°
2. Melting point of acetyl derivative ..	192–93°	197–98°
3. $FeCl_3$ colour reaction	Olive green	Olive green
4. Lead acetate colour reaction ..	Red precipitate	Red precipitate
5. Formula of hydrate	$C_{15}H_{10}O_7$, H_2O	$C_{15}H_{10}O_7$, $2H_2O$

The most remarkable difference between the isomeric pairs exists in their reactions towards alkaline buffer solutions of different pH values. Quercimeritrin and Quercetin give only yellow colours which fade slowly whereas Herbacitrin produces first yellow rapidly changing to emerald green just like Gossypitrin, and Herbacetin gives a bright blue after the initial yellow just like Gossypetin. In these colour reactions the resemblance between Gossypitrin and Herbacitrin, and between Gossypetin and Herbacetin is very close. They resemble also in their colour reactions with ferric chloride and lead acetate. Further a very useful observation in connection with the constitution of the new anthoxanthins is that they give the gossypetone reaction quite similar to Gossypitrin and Gossypetin. From the above reactions and the fact that Herbacitrin occurs in the cotton flowers side by side with Gossypitrin, it was deduced that the new glucoside and aglucone should have constitutions similar to Gossypitrin and Gossypetin as far as the benzopyrone portion of the molecules were concerned, that is, three of the five hydroxyl groups in Herbacetin should be in positions 5, 7 and 8. Since Herbacetin is a flavonol and the 4′-position in the hydroxy-phenyl nucleus is the most favoured among anthoxanthins and anthocyanins, the following constitution was assigned to Herbacetin.



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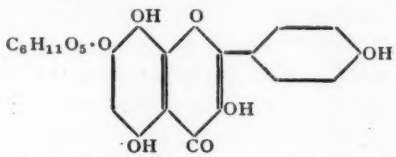

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to what was observed previously. However, on distilling off the alcohol, adding water, removing the remaining alcohol from a water-bath and separating the resin, there slowly crystallised out a considerable amount of a yellow solid (15 g.) which was found to be a mixture of Gossypitrin, Herbacitrin and the aglucones including Quercetin. For separating this mixture an elaborate process of fractional crystallisation had to be adopted using at first boiling water and subsequently dilute alcohol. Gossypitrin was found in the more sparingly soluble fractions and the aglucones Gossypetin, Herbacetin and Quercetin in the more easily soluble fractions whereas Herbacitrin came in between. Consequently the yield of Herbacitrin was considerably reduced (0·7 g.). From the lead acetate and basic lead acetate fractions only the aglucones were obtained.

Crude Herbacitrin was purified by crystallising twice from boiling water and subsequently three or four times from dilute pyridine, when it came out as yellow needles, melting at 247–49°. Further purification did not raise the melting point. This is almost the same as the melting point of Quercimeritrin, but on mixing with Quercimeritrin the melting point was indefinite and lower (232–38°). [Found in air dried specimen : C, 50·5 ; H, 4·9 ; $C_{21}H_{20}O_{12}$, $2H_2O$ required C, 50·4 ; H, 4·8 per cent. Found in specimen dried at 105° *in vacuo* : C, 53·9 ; H, 4·5 ; $C_{21}H_{20}O_{12}$ required C, 54·3 ; H, 4·3 per cent.] The pure substance was insoluble in water and fairly soluble in ethyl alcohol. But the best solvent was pyridine. When aqueous lead acetate was added to an alcoholic solution a red precipitate was obtained which was unchanged on standing or boiling. Ferric chloride gave an olive green colour when added to an alcoholic solution of the pigment and this turned into yellowish green on adding water. When an alkaline solution of the pigment in 50 per cent. potassium hydroxide was left exposed to air for 24 hours, it gave no precipitate on acidification thus showing that it is a flavonol derivative. It gave the Gossypetone reaction with *p*-benzoquinone. When its alcoholic solution was mixed with a similar solution of the quinone, a maroon coloured solid was obtained. This was sparingly soluble in hot water ; the solution was at first blue and subsequently turned brown and on the addition of alkali gave an orange colour rapidly fading to yellow. Lead acetate gave a yellowish brown precipitate and sulphur dioxide regenerated the original pigment.

The colour reactions of *Herbacitrin* in alkaline buffer solutions were as below :

pH	Colour changes
6·8	The solid did not dissolve and remained unaffected for 24 hours.
8·0	Slowly dissolved to a light yellow solution which slowly turned cloudy and green. This was stable for 1 hour. Thereafter it slowly lost colour and after 24 hours was clear and pale brown.
8·6	Solution was complete in five minutes. The yellow changed into a deep emerald green which was rapidly fading. In 10 minutes there was perceptible loss. In ½ hour it turned pale brown and there was no further change for 24 hours.
9·8	Immediately dissolved to a deep yellow solution; in ½ minute became pure emerald green; the colour faded fast and in 10 minutes was pale greenish yellow. After ½ hour it was yellowish brown and after 24 hours very pale brown.
11·0	The changes were much quicker thana bove. The deep green was not obtained. The initial yellow very rapidly (1 minute) went into yellowish green which faded and the solution became almost colourless in ten minutes. No further change was noticed.

The above reactions are fundamentally different from those of Quercimeritrin which are recorded below. However, the resemblance to Gossypitrin (see Neelakantam, Seshadri and Rao[1]) is striking. Probably the loss in colour is a bit faster in the case of Herbacitrin and the absence of deep colour with pH 11·0 is noteworthy.

Quercimeritrin.

pH	Colour changes
6·8	Substance did not dissolve and remained unaffected.
8·0	Dissolved very slowly. After about 24 hours the solution became golden yellow.
8·6	Slowly dissolved (24 hours) to give a golden yellow solution. In 48 hours faded to a very pale yellow.
9·8	Rapidly dissolved. The golden yellow colour was stable for 24 hours. In 48 hours faded to a very pale brown.
11·0	Dissolved immediately to a deep yellow solution. Lost colour in 24 hours.

The above reactions are similar to those given by Quercetin (see below) but the final brown is much weaker.

Herbacitrin octa-acetate was prepared by boiling the pigment with acetic anhydride and sodium acetate. It crystallised from rectified spirits as colourless flat needles and rectangular plates, melting at 214-16°. Mixed melting point with the acetyl derivative of Quercimeritrin was 200-205°. [Found: C, 54·8 ; H, 4·7 ; $C_{37}H_{36}O_{20}$ required C, 55·4 ; H, 4·5 per cent.]

Hydrolysis of Herbacitrin. Preparation of Herbacetin.—Unlike Gossypitrin and Quercimeritrin, Herbacitrin does not give a clear solution on boiling with 7 per cent. aqueous sulphuric acid. So 50 per cent. ethyl alcoholic solution was employed. 0·5 g. of the glucoside was dissolved in 80 c.c. of 50 per cent. ethyl alcohol and enough concentrated sulphuric acid added so as to render the solution 7 per cent. acid and boiled for 3 hours. The turbid solution soon became clear. Alcohol was distilled off and the crystalline yellow precipitate filtered and recrystallised from alcohol. It was thereby obtained as bright yellow flat needles melting at 280-83° darkening a few degrees earlier ; mixed melting point with Quercetin was 250-75°. [Found in air dried specimen : C, 55·6 ; H, 3·9 and loss on drying 5·3, $C_{15}H_{10}O_7$, H_2O requires C, 56·2 ; H, 3·8 ; H_2O, 5·6 per cent. Found in specimen dried at 105° *in vacuo* : C, 58·9 ; H, 3·4 ; $C_{15}H_{10}O_7$ required C, 59·6 ; H, 3·3 per cent.] It gives a deep red precipitate with neutral lead acetate and a dull green colour with ferric chloride. It forms a yellow solution in sulphuric acid devoid of fluorescence and it gives the Gossypetone reaction with *p*-benzoquinone exactly as Gossypetin. The alkali colour reactions were as below:

pH	Colour changes
6·8	The solid was unaffected. After 24 hours there was a tinge of brown in the solution though the solid was apparently undissolved.
8·0	Dissolved very slowly to a light yellow coloured solution. In a few minutes the whole went into a dirty green and then slowly into blue. After ½ hour solution was complete and it was violet blue. This was rather stable and was slowly lost in 24 hours to a pale blue.
8·6	Rapid solution to give a light yellow colour. In a minute it was olive green, in another minute deep violet blue and was fairly stable ; even after 1 hour showed no change. After 24 hours it was colourless.

pH	Colour changes
9·8	Immediate solution to a deep yellow. Faster change (½ minute) to deep blue which was fairly stable ; no change for 1 hour. It lost all colour in 24 hours.
11·0	Much faster changes. Immediate solution to deep yellow, went in a moment to green and then in a second on shaking with air, to blue. No perceptible change for ½ hour. In an hour started fading and in 24 hours complete loss of colour.

There was, therefore, a close resemblance between Herbacetin and Gossypetin (see Neelakantam, Seshadri and Rao[1]). The loss of colour was probably a bit faster with Herbacetin. These reactions are fundamentally different from those given by Quercetin as shown below :

pH	Colour changes
6·8	Unaffected even after 48 hours.
8·0	Slowly dissolved to a yellow solution. Remained cloudy even after 48 hours. After 24 hours still yellow ; after 48 hours yellowish brown.
8·6	Dissolved somewhat faster to a yellow solution, still cloudy. Yellow even after 24 hours. After 48 hours cloudy and faint brown.
9·8	Rapidly dissolved to a clear deep yellow solution. After 24 hours unchanged and after 48 hours yellowish brown.
11·0	Rapidly dissolved to a yellow solution. After 2 hours was deep brown-red and thereafter stable. The colour changes were not prominent. No blue or green colour could be noticed. It closely resembled Quercimeritrin.

The acetyl derivative of Herbacetin (*Herbacetin penta-acetate*) was obtained by boiling the aglucone with acetic anhydride and sodium acetate. It crystallised easily from alcohol as colourless needles and long rectangular plates, melting at 192–3°. [Found : C, 58·0 ; H, 3·9 ; $C_{25}H_{20}O_{12}$ required C, 58·6 ; H, 3·9 per cent.] Mixed melting point with penta-acetyl quercetin was 165-70°.

Oxidation of Herbacitrin. Isolation of Anisic acid.—Herbacitrin (0·5 g.) was treated with 50 per cent. caustic potash (8 c.c.). It dissolved immediately

to a blood red solution which was frequently shaken and kept exposed to air for 48 hours. It became finally opaque and brown. It was acidified and extracted with ether. The ether extract gave a very small quantity of a solid which gave a red colour with ferric chloride. The aqueous solution still contained most of the product and it was therefore again rendered alkaline and shaken with excess of dimethyl sulphate. After shaking for 1 hour it was heated to 100° for a few minutes, acidified and ether extracted, and the ether solution evaporated. A crystalline solid was thereby obtained. It was purified by dissolving in aqueous sodium carbonate and precipitating with hydrochloric acid. When crystallised from aqueous alcohol it was obtained as colourless needles melting at 182–83°. On comparison, it was found to be identical with anisic acid and a mixture of the two melted at the same temperature (182-83°). The mixed melting point with veratric acid was indefinite and lower (145–55°).

Summary.

Herbacitrin, the new flavonol glucoside obtained from *Gossypium herbaceum* (Uppam) has the formula $C_{21}H_{20}O_{12}$. Though isomeric with Quercimeritrin it differs from it in many properties. On hydrolysis it gives glucose and Herbacetin having the formula $C_{15}H_{10}O_7$ which differs from Quercetin in its reactions. In their colour reactions with alkaline buffer solutions and with *p*-benzoquinone Herbacitrin exhibits a very close resemblance to Gossypitrin and Herbacetin to Gossypetin. From these and other considerations Herbacetin has been given the constitution 3 : 5 : 7 : 8 : 4′-pentahydroxy-flavone and Herbacitrin is represented as its 7-glucoside. This has been confirmed by the oxidation of Herbacitrin to *p*-hydroxy-benzoic acid. The flavonol has now been synthesised in the Dyson Perrins Laboratories in Oxford and found to be identical with the natural specimen.

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2. Neelakantam and Seshadri, *Proc. Ind. Acad. Sci.*, A, 1936, **4**, 54.
3. Attree and Perkin, *J.C.S.*, 1927, 234.

ON THE BAND SPECTRUM OF MERCUROUS IODIDE.

By T. S. Subbaraya, B. Nagesha Rao
and
N. A. Narayana Rao.
(From the Department of Physics, Central College, Bangalore, University of Mysore.)

Received April 4, 1937.

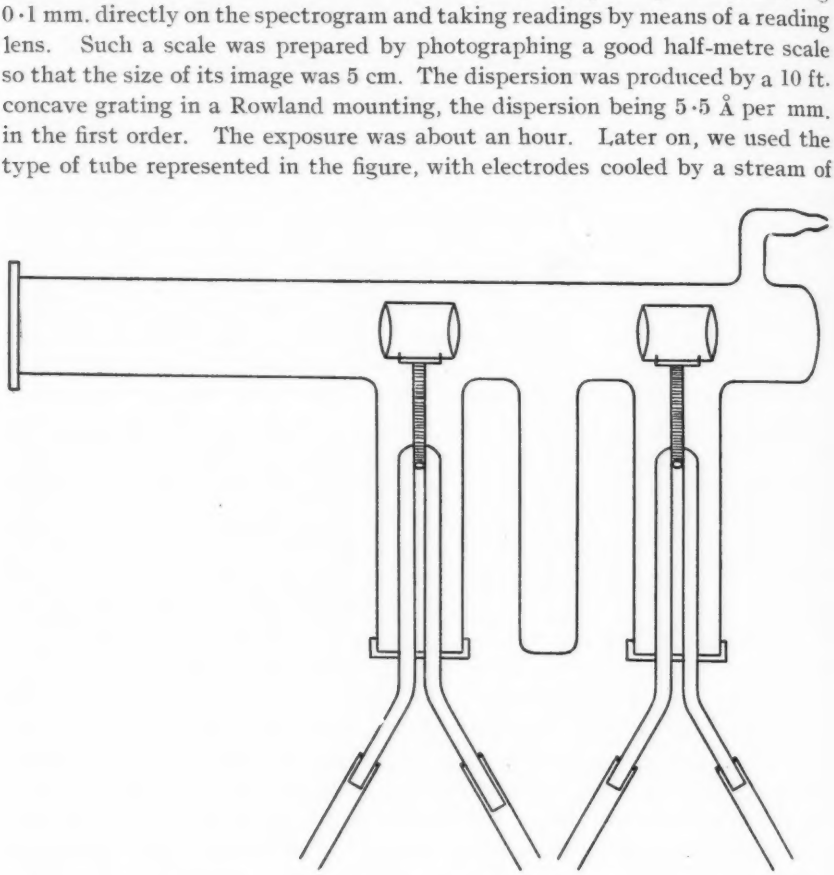
1. Introduction.

The band spectra of the halogenides of zinc, cadmium and mercury have been investigated by a large number of observers. K. Wieland[1] who has observed the various spectra in emission, and has also succeeded in analysing a number of them, gives references to previous observations. According to him, the spectrum emitted by each salt can be divided into three groups denoted by the numerals I, II and III. Group I consists of bands in the ultra-violet with recognizable heads, which can be ascribed to diatomic halogenide molecules. Bands of this group have been analysed by Wieland in the case of HgCl, HgBr and HgI, CdBr and CdI and ZnI. Group II is made up of bands which show little regularity and are ascribed to triatomic molecules. Bands of Group III, which are the subject of this and the following paper, are very faint, diffuse and without sharp heads. In the case of HgI these bands have been observed in fluorescence and measured under low dispersion by A. Terenin[2] and K. Wieland.[3] The values given by them are however discordant. Sponer[4] has attempted to determine the heats of formation of the diatomic and triatomic halogenides on the basis of Wieland's measurements and analysis. Since the bands of Group III play an important part in this determination and yet have not been measured accurately nor properly analysed, we have taken them up for study, and have been able to measure them under high dispersion and also succeeded in arriving at an analysis in the case of HgI and CdI. Our results for HgI are presented in this paper while the next deals with CdI.

2. Experimental.

We have tried various methods of exciting the spectra such as the arc and various types of discharge. The arc spectrum develops the lines in greater intensity to the detriment of the bands, while the electrodeless discharge is too feeble. We obtained successful photographs with a discharge tube energised by a 10,000 volt, $\frac{1}{2}$KW transformer, but the intensity was not

sufficient for the bands to be seen under the microscope. Preliminary measurements correct to 0·02 to 0·05 mm. were obtained by placing a scale reading 0·1 mm. directly on the spectrogram and taking readings by means of a reading lens. Such a scale was prepared by photographing a good half-metre scale so that the size of its image was 5 cm. The dispersion was produced by a 10 ft. concave grating in a Rowland mounting, the dispersion being 5·5 Å per mm. in the first order. The exposure was about an hour. Later on, we used the type of tube represented in the figure, with electrodes cooled by a stream of



water, and a 3KVA transformer giving 2000 volts. We were now able to reduce the slit width to 0·05 mm. and obtained good photographs with exposures ranging between 30 min. and 1 hour. An iron-arc spectrum was always juxtaposed for comparison, by using a Hartmann diaphragm. Ilford hyper-sensitive panchromatic films were used throughout. The bands could now be measured under the microscope. On account of their diffuse nature and the absence of sharp heads, measurements by different observers agreed only to 0·2 Å. The mean wave-lengths given are believed to be correct to within 0·1 Å. With the finer slit each head appears double, and the

measurements refer to the more intense components which are believed to be due to Q-branches, on account of the absence of intense heads and the degradation of the bands to the red. The R-heads do not belong to that Q-head which forms a pair with them but to the preceding Q-head. With this interpretation and the analysis given below, the distance between Q- and R-heads increases with increasing v'' and diminishes with increasing v', as required by the theory developed by Jevons. The measurements for the R-heads are not however given here since their intensity is very low and consequently the values not quite accurate. Another point which requires to be mentioned is that the measurements have been taken at the most intense part of the Q-branches since the heads could not be made out under the microscope.

3. *Results.*

The wave-lengths obtained are given in the table below and they are accurate to about 0·1 Å. They are in agreement with Terenin's measurements within the limits of his accuracy, but Wieland's values do not harmonise with either. The wave-numbers have been obtained from Kayser's *Tabelle der Schwingungszahlen.*

TABLE I.

Intensity	Wave-length	Wave-number	Terenin's Wave-length
3	4488·27	22274·1	..
3	4476·27	22333·8	..
diff. 3	4466·55	22382·4	..
4	4456·05	22435·1	4458
2	4449·44	22468·4	4451
diff. 2 ?	4442·35	22504·3	4444
v. diff. 2	4437·31	22529·9	4433
4	4430·20	22566·0	..
4	4423·64	22599·5	4425
4	4413·14	22653·3	4414

TABLE I—(*Contd.*)

Intensity	Wave-length	Wave-number	Terenin's Wave-length
diff. 3	4402·86	22706·1	4403
2	4392·55	22759·4	..
4	4381·56	22816·5	4382
v. diff. 2	4331·94	23077·9	4333
5	4320·84	23137·2	4322
4	4309·89	23195·9	4313
3	4299·14	23254·0	4301
2	4291·16	23297·2	4290
diff. 3	4282·17	23346·1	4283
diff. 4	4271·28	23405·6	4271
v. diff. 3 ?	4262·60	23453·3	..
3	4260·36	23465·6	4262
3	4251·50	23514·5	4251
2	4241·59	23569·5	4243
1	4225·78	23657·6	4224
3	4213·83	23724·7	4217
2	4204·18	23779·2	4205
2	4193·95	23837·2	4187
1	4169·60	23976·4	4165
3	4159·46	24034·8	..
diff. 2	4148·48	24098·4	4147
3	4139·11	24153·0	..
2	4134·31	24181·0	..
3	4129·28	24210·5	4127

The vibrational analysis of these bands is given in Table II. The analysis shows that these bands have not got any level in common with the systems analysed by Wieland. All attempts at an analysis based on the assumption of a common ground level for these bands and those analysed by Wieland proved to be entirely fruitless. Our analysis shows that one of the levels is a doublet level. Whether the doublet separation is due to the upper level or the lower level cannot be determined indubitably, but it is probable that the lower state is the $^2\Pi$ level to be expected from a combination of the $^1S_0$ state of Hg with the ^2P state of I. The lower level shows a peculiarity which has been previously observed in the hydrides and deuterides of the alkalies and in Hg_2, Cd_2 and Zn_2, namely, that the vibration quanta first increase and then decrease. Another peculiarity observed in Hg_2, Cd_2 and Zn_2, *viz.*, that the vibration levels of the lower term terminate when the vibration quantum attains its initial value (*i.e.*, ω_1') seems to be present here also. The diffuse and weak nature of the bands seems to be due to these peculiarities.

TABLE II.

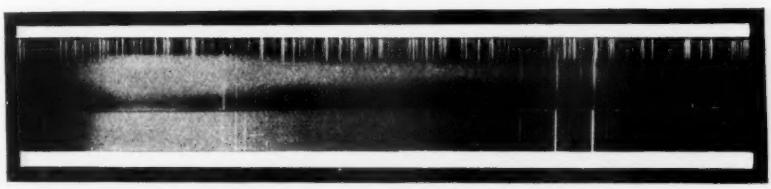
v'	$v''=0$		1		2		3		4		5
0			(23514·5)		(23137·2)		(22759·4)		(22382·4)		
			55·0		*58·7*		*57·1*		*52·7*		
			23569·5	*373·6*	23195·9	*379·4*	22816·5	*381·4*	22435·1		
			267·7		*269·7*				*271·0*		
1	(24153·0)		(23779·2)		(23405·6)				(22653·3)		(22274·1)
	57·5		*58·0*		*60·0*				*52·8*		*59·7*
	24210·5	*373·3*	23837·2	*371·6*	23465·6		23077·9?		22706·1	*372·3*	22333·8
			261·2		*259·1*						*265·7*
2			(24034·8)		(23657·6)						(22599·9)
			63·6		*67·1*						*69·6*
			24098·4	*373·7*	23724·7	*378·6*	23346·1				22599·5
					251·7						
3					23976·4						

4. *Discussion.*

Our analysis of the bands shows that this system (system B in the nomenclature adopted by Wieland) has not got the same lower level as systems C and D analysed by Wieland. He has interpreted the results of his fluorescence experiments on the basis of a common lower level for all these systems. The present analysis, however, is not in contradiction with the fluorescence

data. Thus while systems C and D with ν_{00} at 4·05 and 4·5 volts respectively are excited by light of energy 6·4 and 7·1 volts, giving for the energy available for the dissociation of HgI_2 into HgI and I the values 2·3 and 2·6 volts, Wieland's assumption that system B has the same lower level and that its ν_{00} is at 3·4 volts leaves only 2·1 volts for the dissociation of HgI_2. On the basis of our analysis ν_{00} of system B is at 2·95 volts. We may also assume that the lower state of B splits into Hg $^1S_0$ and I ^2P just as the common lower level of systems C and D is supposed to do. If on the analogy of Hg_2 we also assume that the position of the electronic level corresponds to the point where the vibration quantum is a maximum, the $v'' = 0$ level of system B will be 0·19 volt below the ($^1S_0 + {}^2P$) level. According to Wieland's analysis of system C, its $v'' = 0$ level is 0·5 volts below ($^1S_0 + {}^2P$). Hence $v'' = 0$ of system B is 0·31 volt above the $v'' = 0$ level of system C. Taking this lower level of the system C to be the ground-level, ν_{00} of system B is at 2·95 + 0·31 or 3·26 volts above the ground-level, so that when system B is excited by light of 5·5 volts, the energy available for the dissociation of HgI_2 into HgI + I is 2·24 volts. This value accords better with those obtained from the other systems. The present analysis also removes another difficulty that was associated with the older point of view. Thus in order to explain the appearance of successive differences of about 120 cm.$^{-1}$ between consecutive bands, Wieland assumes that 120 cm.$^{-1}$ represents the vibration frequency of the ground-level and that the difference 180 cm.$^{-1}$ appearing later is the vibration frequency of the upper state, and yet he assumes that the upper potential curve is shifted to longer wave-lengths as compared with the lower curve. This assumption is therefore in direct contradiction with Morse's rule. In the case of the analysis presented here, ω'' is larger than ω' and the intensity distribution gives a Condon parabola which corresponds to the case of ω'' being larger than ω'. The difficulty that was experienced in interpreting the system B is due to the peculiar behaviour of the lower level. Mulliken[5] has recently discussed the type of potential curve which will represent such a level. But his results are qualitative and their application to the present case is not quite clear. So we have refrained from drawing potential curves or representing our results by formulæ. Our analysis of the system B of CdI, to be presented in the following paper, shows that the peculiar behaviour of the lower state is common to HgI and CdI. The connection between this behaviour and the difficulties met with in the discussion of the type of binding into which an atom in a $^1S_0$ state can enter requires further investigation for its elucidation.

In conclusion, we should like to express our best thanks to Prof. B. Venkatesachar for his kind encouragement and many helpful suggestions.



A 2000 volt 3 KVA Transformer Discharge; Slit width 0·05 mm.
B 10000 volt ½ KW Transformer Discharge; Slit width 0·08 mm.
The doubling of some of the bands can be made out in A.

One of us (B. N.) is indebted to the University of Mysore for a scholarship which made it possible for him to take part in this work.

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ON THE BAND SPECTRUM OF CADMIUM IODIDE.

By T. S. Subbaraya, N. A. Narayana Rao
and
B. Nagesha Rao.

(From the Department of Physics, Central College, Bangalore, University of Mysore.)

Received April 4, 1937.

1. *Introduction.*

In the foregoing paper we presented the results obtained during an investigation of the group III bands of mercury iodide. The present paper deals with the similar results obtained with cadmium iodide. As in the case of mercury iodide, Wieland[1] obtained bands of group III in emission, but was not able to determine their wave-lengths. He observed, however, that the bands followed at intervals of about 18 to 20 Å and that after groups of five or six bands there occurred places where the band structure was almost washed out. Oeser[2] has obtained the bands in fluorescence, but the small dispersion employed by him did not allow of sufficient accuracy being attained in the wave-length measurements. In view of the importance of bands of group III for the problem of the heats of dissociation, we have taken up a study of them. Their regular succession at almost equal intervals and their diffuseness suggested a close resemblance to the bands of Hg_2 observed by Lord Rayleigh[3] and also to the spectra of Se_2 and Te_2. One of us[4] has analysed the bands of Hg_2, Cd_2 and Zn_2 and found a peculiarity in the lowest state, *viz.*, that the vibration quanta first increase and then decrease. The result of the present investigation shows that the external similarity between the spectra of these molecules and the group III bands of the Hg, Cd and Zn halides is reflected also in the behaviour of the lower level of the latter bands as compared with the ground level of Hg_2, Cd_2 and Zn_2.

2. *Experimental.*

We have used different sources for getting the bands with sufficient intensity. A vacuum arc with three limbs, the two outer having electrodes and containing cadmium, and the middle containing CdI_2, gave a bright spectrum of the bands when the CdI_2 was heated and a good photograph was obtained

with Hilger's E_1 spectrograph. The cadmium, however, soon affected the pyrex glass and when the arc once went out (which was usually in about 20 minutes), the tube cracked and no further exposure was possible. On account of the diffuse nature of the bands we could not get accurate wave-lengths with a spectrum obtained by means of the E_1 spectrograph. We later on used the type of tube figured in the previous paper, having electrodes cooled by a stream of water and energised by a $\frac{1}{2}$ KW, 10,000 volt transformer. With this source and a 10 ft. concave grating in a Rowland mounting, having a dispersion of 5·5 Å. per mm. in the first order, we obtained good photographs in about half an hour, but longer exposures were not practicable since the substance got exhausted very rapidly. The bands were most intense when the discharge had a whitish yellow colour. An iron arc was juxtaposed without using a condensing lens so that second order lines have appeared and made up for paucity of lines in the red region of the iron spectrum. Although we could see the bands very well as is seen from the reproduction, they could not be measured under the microscope when the usual magnification was employed. Accordingly the magnification was reduced by removing the eye-piece and putting the cross wires farther down the microscope tube. Measurements were also taken on a microphotometer tracing of the bands. In both cases different measurements agreed with one another to within 1 Å and the final wave-lengths must be correct to within 0·5 Å or better. No heads however can be recognised and so readings have been taken for the centre of each band. The wave-numbers are also correct to within 1 cm.$^{-1}$ but common differences differ somewhat more than 2 cm.$^{-1}$ on account of the difficulty of locating the corresponding points in different bands.

3. *Results.*

The final wave-lengths are given in Table I. The degree of accuracy reached is sufficient to arrive at definite conclusions regarding some assumptions made by previous workers. The bands of group III have been assumed to have the same lower level as those of group I analysed by Wieland. An attempt at analysis on this basis was found to be futile, and the final analysis presented here was suggested by the wash-out of the bands at intervals of five or six. According to this analysis presented in Table II, the lower level shows the peculiarity of vibration quanta which first increase and then decrease, just as in the case of HgI, but the actual value of the vibration frequency in the lower state, is far smaller than that of the upper state, whereas in HgI the lower state has the higher frequency. This difference accounts for the difference in the appearance of the bands. No doublet structure has been found in CdI whereas HgI exhibits such a doublet

structure. The reason might be that the doublet interval is too small, as is to be expected.

TABLE I.

Int.	Wave-length	Wave-number	Int.	Wave-length	Wave-number
1	6340·57	15767·1	1	5988·13	16695·1
1	21·17	15815·5	1	71·07	16742·8
2	01·84	15864·0	1	52·58	16794·8
2	6283·22	15911·0	2	5936·64	16839·9
2	64·33	15959·0	2	19·90	16887·5
1	44·40	16009·9	2	02·67	16936·8
?	22·06	16067·4	2	5885·37	16986·6
?	01·38	16121·0	2	68·85	17034·4
1	6187·10	16158·2	1	51·91	17083·7
3	68·28	16207·5	1	35·79	17130·9
3	49·65	16256·6	2	20·16	17176·9
2	31·96	16303·5	2	04·11	17224·4
2	13·10	16353·8	3	5787·41	17274·1
?	6096·99	16397·0	2	70·61	17324·4
1	76·83	16451·4	1	54·86	17371·8
2	58·46	16501·3	1	39·07	17419·6
2	41·28	16548·2	?	24·48	17464·0
2	23·16	16598·0	1	09·44	17510·0
1	05·75	16646·1	1	5693·35	17559·5

TABLE II.

v'	$v''=0$		1		2		3		4		5		6
0	..		..		..		..		..		..		..
1	..		..		..		..		..		..		..
2	(16067·4)		(16009·9)		15959·0	*48·0*	15911·0	*47·0*	15864·0	*48·5*	15815·5	*48·4*	15767·1
			343·9		*344·5*		*345·6*		*343·5*		*342·7*		
3	(16397·0)		16353·8	*50·3*	16303·5	*46·9*	16256·6	*49·1*	16207·5	*49·3*	16158·2		(16121·0)
			341·3		*342·6*		*341·4*		*340·7*		*343·1*		
4	16742·8	*47·7*	16695·1	*49·0*	16646·1	*48·1*	16598·0	*49·8*	16548·2	*46·9*	16501·3		(16451·4)
	340·9		*339·3*		*340·5*		*338·8*		*339·3*		*338·6*		
5	17083·7	*49·3*	17034·4	*47·8*	16986·6	*49·8*	16936·8	*49·3*	16887·5	*47·6*	16839·9	*45·1*	16794·8
	335·9		*337·4*		*337·8*		*337·3*		*336·9*		*337·0*		*336·1*
6	17419·6	*47·8*	17371·8	*47·4*	17324·4	*50·3*	17274·1	*49·7*	17224·4	*47·5*	17176·9	*46·0*	17130·9
									335·1		*333·1*		*333·1*
7									17559·5	*49·5*	17510·0	*46·0*	17464·0

Note.—The bands with $v' = 0$ and $v' = 1$ could not be measured since the continuum masked them. In the photograph taken with the E_1 spectrograph the last measured band was 15118 cm.$^{-1}$ corresponding to $v' = 0$, $v'' = 5$. There exist no bands beyond $v'' = 6$ for any value of v'. This termination of the bands at a particular value of v'' is characteristic of the peculiar lower state.

As explained in the previous paper, we have refrained here also from attempting to represent our results by a formula since the peculiar ground state does not allow this to be done. An interpretation of Oeser's fluorescence data is left for future consideration.

Finally, the important point brought out by these investigations is that the lower level of system B in CdI and HgI shows the peculiarity previously observed by one of the authors[1] in Hg_2, Cd_2 and Zn_2, *viz.*, that the vibration frequencies first increase and then decrease, and the vibration levels terminate when the vibration frequency becomes equal to what it was between the 0th and 1st vibration levels.

In conclusion, we should like to record our best thanks to Prof. B. Venkatesachar for the many helpful suggestions with which he has

favoured us. One of us (B.N.) is indebted to the University of Mysore for the grant of a scholarship.

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Cd I
Fe
Sodium Doublet
6438
(Taken with 10 ft. Concave Grating)

Taken with Hilger (E_1) Spectrograph
Sodium Doublet
6438

DERIVATIVES OF SALICYLIC ACID.

Part XII. Nitro-Salicylic Acids and their Methyl Ethers.

By N. W. Hirwe and (Miss) K. D. Gavanker.
(*From the Royal Institute of Science, Bombay.*)

Received March 19, 1937.
(Communicated by Dr. T. S. Wheeler, Ph.D., F.I.C., F.Inst.P., M.I.Chem.E.)

Investigation of the nitro-salicylic acids* has been here continued as their amides and the amides of their methyl ethers were required for a study of their chloralamides. A new method for the synthesis of 3 : 5-dinitro-salicylic acid by nitration of salicylic acid is described ; it gives a better yield and does not require the same temperature control as the method of Meldola, Foster and Brightman.[1]

The 3 : nitro and 5 : nitro-salicylic acids give a red colour with ferric chloride ; the 3 : 5-dinitro-salicylic-acid responds to the test feebly, though its ester and amide give deep red colours.

Unlike the 3 : bromo-salicylic acid, the 3 : nitro-acid, like ortho-cresotic acid, yields an ester by simple alcoholysis. The phenolic group in these three acids is not affected by the phosphorus pentachloride ; like the 3 : bromo-acid, no amide of 3 : nitro-salicylic acid could be obtained through the phosphorus pentachloride reaction.

The methyl ethers of these acids are unstable, and the instability is more pronounced with increase in the number of nitro groups. Thus the methyl ethers of 3 : nitro- and 5 : nitro-salicylic acids are hydrolysed by warm but not by cold alkali ; while that of 3 : 5-dinitro-salicylic acid is easily hydrolysed by cold alkali. It has thus not been possible to prepare these methyl ethers by direct methylation. These have therefore been prepared by the direct nitration of the methyl ethers of salicylic acid.

The method of Froelicher and Cohen[2] is found to be better for the 3 : nitro-2-methoxy-benzoic acid, while that of Simonsen and Rau,[3] coupled with a new modification for the separation of the two isomeric acids, works well for the preparation of 5 : nitro-2-methoxy-benzoic acid. A new method has been described for the preparation of 3 : 5-dinitro-2-methoxy-benzoic acid from the *O*-methoxy-benzoic acid by direct nitration.

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* Meldrum and Hirwe, *J. Ind. Chem. Soc.*, 1928, **5**, 95.

Experimental.

3 : *Nitro-salicylic acid*—was prepared according to Meldrum and Hirwe (*loc. cit.*).

Calcium-3-nitro-salicylate—crystallised from hot water in needles with two molecules of water. [Found : H_2O, 8·5 ; Ca, 9·1 ; $C_{14}H_8O_{10}N_2Ca$, $2H_2O$ requires H_2O, 8·2 ; Ca, 9·1 per cent.]

5 : *Nitro-salicylic-acid*—was prepared according to Meldrum and Hirwe (*loc. cit.*).

Sodium-5-nitro-salicylate—crystallises from water in yellow microscopic needles with one molecules of water. [Found : H_2O, 8·2 ; Na, 10·3 ; $C_7H_4O_5NNa$, H_2O requires H_2O, 8·1 ; Na, 10·3 per cent.]

3 : *Nitro-2-methoxy-benzoic acid*—was prepared according to Froelicher and Cohen.[2]

Calcium-3-nitro-2-methoxy benzoate—crystallised from water in yellow cubic plates. [Found : Ca, 9·0 ; $C_{16}H_{12}O_{10}N_2Ca$ requires Ca, 9·3 per cent.]

Barium-3-nitro-2-methoxy-benzoate—crystallised from water in yellow needles with four molecues of water, which could not be removed as the compound decomposes on heating. [Found : Ba, 22·6 ; $C_{16}H_{12}O_{10}N_2Ba$, $4H_2O$ requires Ba, 22·8 per cent.]

Sodium-3-nitro-2-methoxy-benzoate—crystallised from water in yellowish crystals with three molecules of water. [Found : H_2O, 19·6 ; Na, 8·3 ; $C_8H_6O_5$ NNa, $3H_2O$ requires H_2O, 19·8 ; Na, 8·4 per cent.]

Methyl-3-nitro-2-methoxy-benzoate.—A mixture of 3 : nitro-2-methoxy-benzoic acid (5 g.), alcohol (absolute ; 20 c.c.) and sulphuric acid (conc. 4 c.c.) was kept for twelve hours and heated under reflux for five hours ; on dilution a solid was obtained which, crystallised from alcohol in white needles, m.p. 60°. [Found : N, 6·8 ; $C_9H_9O_5N$ requires N, 6·6 per cent.]

3 : *Nitro-2-methoxy-benzamide.*—A mixture of 3 : nitro-2-methoxy-benzoic acid (10 g.) and phosphorus pentachloride (15 g.) was heated on a water-bath until a clear liquid is obtained, which on being poured into strong ammonia (sp. gr., 0·888) gave a solid which crystallised from water in yellowish needles, m.p. 124°. [Found : N, 14·3 ; $C_8H_8O_4N_2$ requires N, 14·3 per cent.]

5 : *Nitro-2-methoxy-benzoic acid*—the nitration was carried out according to Simonsen and Rau.[3] M.p. = 160°–161°.

Method for separation.—The mixture of 3 : nitro-2-methoxy and 5 : nitro-2-methoxy-benzoic acids obtained in the nitration of the 2 : methoxy-benzoic acid was neutralised with hot potassium carbonate solution. Potassium-

5-nitro-2-methoxy-benzoate being less soluble separated and was filtered off. On acidification of this salt an acid was obtained. (M.p. *vide* Sim. and Rau ; Fro. and Coh.).

3 : *Nitro-2-methoxy-benzoic acid*—the filtrate obtained in the above experiment was acidified, and the acid obtained was recrystallised from acetic acid, m.p. 196° (194°–96° ; Fro. and Coh.).

Sodium-5-nitro-2-methoxy-benzoate—crystallised from water in yellowish needles, with one molecule of water. [Found : H_2O, 7·3 ; Na, 9·5 ; $C_8H_6O_5NNa$ requires H_2O, 7·6 ; Na, 9·7 per cent.]

Ethyl-5-nitro-2-methoxy-benzoate.—A mixture of 5-nitro-2-methoxy-benzoic acid (5 g.), absolute alcohol (20 c.c.) and sulphuric acid (conc. 4 g.) was heated under reflux for five hours ; the ester separated on dilution, was crystallised from alcohol in white needles, m.p. 80°–81°. [Found : N, 6·4 ; $C_{10}H_{11}O_5N$ requires N, 6·2 per cent.]

Potassium-5-nitro-2-methoxybenzoate—crystallised from water in yellowish needles, with one molecule of water. [Found : H_2O, 6·8 ; K, 15·4 ; $C_8H_6O_5NK$, H_2O requires H_2O, 7·1 ; K, 15·4 per cent.]

5 : *Nitro-2-methoxy-benzamide* —A mixture of the acid (20 g.) and phosphorus pentachloride (20 g.) was heated on the water-bath until a clear liquid was obtained. The solid formed, on pouring it in strong ammonia, was crystallised from acetic acid in yellow plates, m.p. 213°. [Found : N, 14·1 ; $C_8H_8O_4N_2$ requires N, 14·3 per cent.]

3 : 5-*Dinitro-salicylic acid.*—To a solution of salicylic acid (20 g.) in sulphuric acid (conc. 153 g.), fuming nitric acid (sp. gr. 1·45 ; 25 g.) was gradually added keeping the temperature below 25°. The reaction was completed at 40°. The mixture was poured on to crushed ice and the resulting solid was crystallised from water in yellow needles, m.p. 172°–173° (173°– Salkowsky[4] ; 173°– Meldola, Foster and Brightman.)[1] It gives a faint red tinge with ferric chloride.

Ethyl : 3 : 5-*Dinitro-salicylate.*—A mixture of the acid (5 g.), absolute alcohol (20 c.c.) and sulphuric acid (conc. 4 c.c.) was treated as before for esterification. The ester was crystallised from alcohol in yellow needles, m.p. 98–99° (98–99° Cahours).[5] It gives red colour with ferric chloride.

3 : 5-*Dinitro-salicylamide.*—A solution of the ester (75 g.) in alcohol (100 cc.) was mechanically shaken with strong ammonia (800 c.c., sp. gr. 0·888). The resulting spongy solid gave the amide on acidification, yield 50 g. It was recrystallised from hot water in yellow needles, m.p. 181°. [Found : N, 18·3 ; $C_7H_5O_6N_3$ requires N, 18·5 per cent.). It gives red colour with ferric chloride.

3 : 5-*Dinitro*-2-*methoxy-benzoic acid*.—Nitric acid (sp. gr. 1·45 ; 60 g.) was gradually added to a mixture of methyl-ether of salicylic acid (50 g.) and sulphuric acid (conc. 380 g.) keeping the temperature below 30°. After one hour it was poured on to crushed ice, when a white solid was obtained. It was recrystallised from water. White needles with m.p. 165°-166° (165°, Ullmann[6]).

Barium 3 : 5-*dinitro*-2-*methoxy-benzoate*—crystallises from water in orange microscopic needles, with one mol. of water. (Found : H_2O, 3·1 ; Ba, 21·4 ; $C_{16}H_{10}O_{14}N_4Ba,H_2O$ requires H_2O, 2·8 ; Ba, 21·5 per cent.).

Calcium 3 : 5-*dinitro*-2-*methoxy-benzoate*—crystallised from water in yellow cubes with one molecule of water. [Found : H_2O, 3·2 ; Ca, 7·2 ; $C_{16}H_{10}O_{14}N_4Ca$, H_2O requires H_2O, 3·3 ; Ca, 7·4 per cent.)

3 : 5-*Dinitro*-2-*methoxy-benzamide*.—After heating to a clear liquid the mixture of phosphorus pentachloride (5 g.) and the acid (5 g.) was poured in strong ammonia as before, which gave a solid. It crystallised from water in yellow needles, m.p. 166–67°. [Found : N, 17·7 ; $C_8H_7O_6N_3$ requires N, 17·4 per cent.]

3 : *Nitro-salicylamide*—was prepared according to Meldrum and Hirwe (*loc. cit.*).

3 : *Nitro*-5-*bromo-salicylamide*.—An acetic acid solution of bromine (5 g.) was gradually added to the 3 : nitro-salicylamide (10 g.) in acetic acid and the resulting mixture was poured in water and the required bromo-amide crystallised from acetic acid in needles, m.p. 221°. [Found : N, 10·7 ; Br, 30·5 ; $C_7H_5O_4N_2Br$ requires N, 10·7 ; Br, 30·7 per cent.]

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ON A CONJECTURE OF CHOWLA.

By Dr. Hansraj Gupta.

(From the Government College, Hoshiarpur.)

Received March 23, 1937.

(Communicated by Dr. S. Chowla.)

1. Corresponding to every prime $p \geqslant 1$, $p \neq 2, 3$; there is an integer P given by the relation :

$$P = P(p) = \frac{p^2 - 1}{24}.$$

It is easy to prove that excepting P (5), *i.e.*, 1,
every $P \equiv 0$, or 2 (mod. 5).

If $P \equiv 0$ (mod. 5), denote P/5 by A, and

If $P \equiv 2$ (mod. 5), denote $(P - 2)/5$ by B.

The A's and the B's < 2000, are listed in section 4.

Under C are listed all those numbers upto 2000, which can be formed by adding together an A and a B.

I find that every positive integer $i \leqslant 2000$, can be expressed as the sum of an A and a C, and also as the sum of a B and a C.

This leads me to

Conjecture 1. Every positive integer j which is $\equiv 2$, or 4 (mod. 5), can be expressed as the sum of three P's. If conjecture 1 be true, it shall follow that every positive integer can be expressed as the sum of four P's.

Since all positive integers $\leqslant 23$, can be expressed as the sums of at the most four squares of primes, we readily see that I. Chowla's Conjecture,[1] *viz.*, "Every positive integer can be expressed as the sum of at the most eight squares of primes $p \geqslant 1$;" is contained in Conjecture 1.

2. The following conjecture is noteworthy.

Conjecture 2. Almost all integers which cannot be expressed as the sums of less than four P's are $\equiv 3$ (mod. 5).

If we exclude the use of P (5), *i.e.*, 1, no number of the form $5n + 3$, can be expressed as the sum of less than four P's. Hence only those of the numbers m, of the form $5n + 3$, can be expressed as the sums of less than four P's, for which $(m - 3)/5$ is a C.

Most of the numbers can be expressed as the sums of three A's and also as the sums of three B's. Hence there are only a few numbers of the forms $5n$, and $5n + 1$, which cannot be expressed as the sums of less than four P's. These numbers are listed under D in section 4.

3. In view of Conjecture 1, Chowla's conjecture stands verified[2] for all numbers upto 240000. The following are some of the interesting results which depend upon Conjectures 1 and 2.

(i) Every positive integer of the form $24n + 4$ can be expressed as the sum of four squares of primes.

(ii) Every positive integer of the form $120n + 51$, or $120n + 99$, can be expressed as the sum of three squares of primes.

(iii) The number[3] of positive integers $\leqslant k$, which cannot be expressed as the sums of less than four P's, is $< k/5$.

(iv) The number of positive integers less than k, which cannot be expressed as the sums of less than eight squares of primes, is $< k/20$.

4. The A's < 2000 are :

0, 1, 3, 7, 8, 14, 29, 31, 42, 52, 66, 85, 99, 143, 161, 185, 190, 267, 273, 304, 330, 371, 437, 476, 484, 525, 603, 612, 658, 806, 913, 1015, 1074, 1197, 1261, 1340, 1394, 1463, 1477, 1548, 1606, 1680, 1771, 1912.

The B's < 2000 are :

0, 1, 2, 4, 11, 15, 18, 23, 37, 44, 57, 78, 88, 95, 106, 134, 156, 205, 221, 232, 249, 310, 323, 414, 429, 452, 550, 576, 639, 667, 715, 785, 816, 837, 946, 1003, 1038, 1122, 1159, 1222, 1313, 1562, 1635, 1740, 1786, 1817, 1976.

The C's are listed below :

0, 1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 14, 15, 16, 18, 19, 21, 22, 23, 24, 25, 26, 29, 30, 31, 32, 33, 35, 37, 38, 40, 42, 43, 44, 45, 46, 47, 49, 51, 52, 53, 54, 56, 57, 58, 60, 63, 64, 65, 66, 67, 68, 70, 71, 73, 75, 77, 78, 79, 81, 84, 85, 86, 87, 88, 89, 91, 92, 95, 96, 98, 99 ;

1 00, 01, 02, 03, 06, 07, 08, 09, 10, 13, 14, 17, 19, 20, 22, 23, 24, 26, 29, 30, 34, 35, 36, 37, 40, 41, 42, 43, 44, 45, 47, 48, 54, 56, 57, 58, 59, 61, 62, 63, 64, 65, 66, 70, 72, 73, 76, 77, 79, 80, 84, 85, 86, 87, 89, 90, 91, 92, 94, 96, 98 ;

2 00, 01, 03, 05, 06, 08, 12, 13, 18, 19, 21, 22, 24, 27, 28, 29, 31, 32, 33, 34, 35, 36, 38, 39, 40, 41, 42, 46, 47, 49, 50, 52, 55, 56, 57, 61, 63, 67, 68, 69, 71, 73, 74, 75, 77, 78, 80, 82, 84, 85, 87, 88, 90, 91, 95, 96, 98, 99 ;

3 01, 04, 05, 06, 08, 10, 11, 13, 15, 17, 18, 19, 20, 22, 23, 24, 26, 27, 30, 31, 32, 34, 37, 39, 41, 45, 46, 48, 51, 52, 53, 54, 55, 61, 62, 64, 65, 66, 67, 68, 71, 72, 73, 74, 75, 76, 79, 82, 86, 87, 89, 90, 92, 93, 94, 95, 99 ;

4 01, 06, 07, 08, 09, 10, 11, 14, 15, 17, 18, 21, 22, 23, 25, 28, 29, 30, 32, 34, 36, 37, 38, 39, 41, 43, 45, 48, 49, 52, 53, 55, 56, 58, 59, 60, 64, 66, 71, 72, 74, 76, 77, 78, 80, 81, 83, 84, 85, 86, 87, 88, 91, 94, 95, 99 ;

5 00, 02, 04, 05, 07, 08, 09, 13, 14, 15, 16, 18, 20, 21, 22, 25, 26, 27, 28, 29, 32, 33, 35, 36, 37, 40, 41, 43, 48, 50, 51, 53, 54, 57, 58, 62, 64, 69, 71, 72, 75, 76, 77, 79, 81, 82, 83, 84, 90, 92, 93, 95, 96, 99 ;

6 02, 03, 04, 05, 07, 10, 12, 13, 14, 16, 18, 19, 20, 21, 23, 26, 27, 28, 30, 31, 32, 35, 37, 39, 40, 42, 46, 47, 49, 53, 56, 58, 59, 60, 61, 62, 67, 68, 69, 70, 73, 74, 75, 76, 81, 86, 87, 89, 90, 91, 93, 94, 95, 96, 97, 98 ;

7 00, 02, 05, 07, 08, 09, 11, 15, 16, 18, 19, 22, 23, 24, 25, 29, 30, 33, 35, 36, 37, 38, 40, 44, 46, 47, 52, 53, 56, 57, 59, 60, 61, 64, 66, 67, 68, 74, 81, 82, 85, 86, 88, 92, 93, 94, 99 ;

8 00, 06, 07, 08, 10, 14, 16, 17, 19, 21, 23, 24, 27, 28, 29, 30, 33, 35, 37, 38, 40, 43, 44, 45, 47, 48, 49, 50, 51, 52, 54, 57, 58, 61, 63, 66, 68, 70, 76, 79, 80, 82, 84, 89, 90, 94, 98 ;

9 00, 01, 03, 05, 06, 07, 12, 13, 14, 15, 17, 21, 22, 24, 26, 28, 31, 34, 35, 36, 39, 40, 43, 46, 47, 49, 50, 53, 54, 57, 59, 60, 62, 68, 69, 70, 71, 75, 77, 80, 81, 82, 87, 88, 91, 97, 98 ;

10 01, 03, 04, 06, 08, 10, 11, 12, 13, 15, 16, 17, 19, 22, 26, 27, 30, 31, 32, 33, 34, 38, 39, 41, 45, 46, 47, 52, 55, 58, 59, 60, 64, 67, 69, 72, 74, 75, 76, 78, 80, 83, 85, 86, 87, 88, 89, 90, 92, 93, 97 ;

11 01, 02, 03, 04, 07, 10, 11, 15, 16, 18, 20, 21, 22, 23, 25, 29, 30, 31, 34, 36, 37, 41, 43, 45, 46, 49, 51, 52, 53, 56, 59, 60, 62, 64, 66, 67, 69, 71, 73, 74, 79, 80, 81, 87, 88, 90, 91, 92, 93, 97, 98, 99 ;

12 01, 07, 08, 11, 12, 13, 15, 19, 20, 21, 22, 23, 25, 28, 29, 30, 34, 35, 36, 40, 41, 42, 44, 47, 50, 51, 53, 54, 58, 61, 62, 63, 64, 65, 69, 70, 72, 74, 75, 76, 79, 83, 84, 85, 88, 92, 95, 97, 98 ;

13 00, 02, 03, 05, 06, 07, 10, 11, 12, 13, 14, 16, 17, 18, 20, 21, 23, 25, 27, 31, 33, 38, 39, 40, 41, 42, 44, 49, 51, 53, 55, 56, 58, 62, 63, 65, 67, 68, 73, 74, 77, 79, 82, 83, 84, 88, 89, 94, 95, 96, 97, 98 ;

14 02, 05, 07, 09, 12, 17, 18, 19, 22, 26, 28, 29, 30, 31, 32, 35, 38, 40, 43, 44, 45, 46, 49, 51, 52, 56, 63, 64, 65, 66, 67, 71, 72, 73, 74, 75, 77, 78, 79, 81, 82, 86, 87, 88, 89, 92, 93, 95, 96, 98 ;

15 00, 03, 07, 10, 14, 20, 21, 22, 26, 28, 30, 34, 41, 45, 48, 49, 50, 51, 52, 55, 58, 59, 61, 62, 63, 65, 66, 69, 70, 71, 72, 76, 80, 83, 84, 85, 86, 89, 91, 92, 93, 96, 97, 98, 99 ;

16 04, 05, 06, 07, 08, 10, 11, 14, 15, 17, 19, 21, 22, 24, 26, 28, 29, 33, 35, 36, 38, 41, 42, 43, 47, 49, 50, 54, 59, 61, 63, 64, 66, 68, 75, 77, 80, 81, 82, 84, 87, 90, 91, 94, 95, 96, 98 ;

17 01, 03, 04, 05, 06, 09, 12, 13, 17, 20, 23, 24, 25, 26, 29, 30, 34, 37, 40, 41, 43, 47, 48, 50, 52, 53, 54, 58, 62, 68, 69, 71, 72, 73, 75, 78, 80, 82, 86, 87, 89, 92, 93, 94, 96, 97 ;

18 00, 06, 08, 09, 11, 14, 15, 17, 18, 20, 23, 24, 25, 27, 28, 29, 31, 34, 35, 36, 37, 38, 39, 44, 46, 48, 49, 52, 55, 58, 59, 64, 66, 69, 71, 77, 80, 83, 85, 90, 91, 92 ;

19 00, 01, 02, 05, 06, 08, 11, 12, 13, 14, 15, 16, 23, 25, 27, 28, 29, 30, 33, 35, 39, 44, 47, 49, 51, 56, 60, 61, 62, 65, 69, 70, 71, 76, 77, 78, 79, 82, 83, 84, 90, 92, 99 ;

20 00.

The following are the D's :

1125, 1310, 1360, 1936, 1971, 2245, 3895, 5000, 5055, 5066, 6270, 6501, 6540, 6920, 8055.

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3. For $k = 10000$, this is > 1000.

41 1-37—Printed at the Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent, and Published by The Indian Academy of Sciences, Bangalore.